

Digitized by the Internet Archive in 2010 with funding from University of Toronto

# THE HOME CANADIAN INSTITUTE



URNAL OF

# ANKLIN INSTITUTE

DEVOTED TO

# SCIENCE AND THE MECHANIC ARTS

EDITED BY R. B. OWENS, E.E., M.A., D.Sc., F.R.S.C.

#### Associate Editors:

BRIG. GEN. JAMES ALLEN WILDER D. BANCROFT, PH.D. HARRY F. KELLER, PH.D. JOHN J. CARTY A. S. CUSHMAN, PH.D. LOUIS DUNCAN, PH.D. W. J. HUMPHREYS, PH.D.

HARRY C. JONES, PH.D. ALFRED NOBLE, LL.D. L. A. OSBORNE, M.E. EDGAR F. SMITH, PH.D. R. S. WOODWARD, PH.D. LT. COL. GEO. O. SQUIER, PH.D. A. F. ZAHM, PH.D.

C. P. STEINMETZ, PH.D. S. W. STRATTON, SC.D. NAVAL CON. D. W. TAYLOR S. M. VAUCLAIN, SC.D.

COMMITTEE ON PUBLICATIONS: LOUIS E. LEVY, CHAIRMAN

GEORGE A. HOADLEY

JOHN BIRKINBINE

W. C. L. EGLIN E. H. SANBORN

VOL. CLXXVI.—Nos. 1051-1056 (88th YEAR)

JULY-DECEMBER, 1913

PHILADELPHIA

Published by the Institute, at the Hall, 15 South Seventh Street.

T F8 V.176 621368 24.10.55

# **JOURNAL**

OF

# THE FRANKLIN INSTITUTE

DEVOTED TO SCIENCE AND THE MECHANIC ARTS

Vol. CLXXVI

JULY, 1913

No. 1

#### INDUSTRIAL COMBUSTIBLE GASES.\*

BY

#### J. M. RUSBY, M.E.,

Engineer of Tests, The United Gas Improvement Company.

Member of the Institute.

This paper is intended to present—with some general prefatory remarks—an outline of the qualities and origin, or method of production, of the most important gases used in the arts, etc. The subject is a wide one, and for at all detailed treatment of its various subdivisions a volume, or even volumes, would be required. This treatment must, therefore, be brief. It is made as non-technical as compatible with clear understanding. Sufficient figures and descriptions of apparatus are given, however, to illustrate the chief demands of the art and the methods of meeting them. The particular designs of apparatus that are used for the production of each of the various gases are exceedingly numerous, and the quality of gas yielded is apt to vary somewhat according to this particular design, or even its method of operation; the illustrations chosen will, however, pretty accurately represent the general subject.

<sup>\*</sup> Presented at the meeting of the Mechanical and Engineering Section held Thursday, April 24, 1913.

<sup>[</sup>Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.]

Copyright, 1913, by The Franklin Institute.

It is probable that nothing will be given which is new to those having even a fair acquaintance with the gas business. To others who are not thus familiar, however, it is hoped to present an outline of the general subject which, because of its brevity, scope, and simplicity of treatment, will be easily read and of interest.

The special merits of gaseous fuel, which indicate the advantages obtained by the gasification of solid—and to some extent even liquid—fuels, are the following. It is easily transportable and capable of subdivision and use in even the smallest quantity. It is quickly combustible, and its flame, and consequently heat of combustion, capable of concentration. Undesirable impurities. which are incapable of removal from the solid or liquid fuels, can be purified out from their cooled gases, which in many processes is of great importance. It is easily combustible without smoke production. It is also possible to form from a solid or liquid fuel a gas having a greater heat of combustion, and consequently higher flame temperature, than the solid or liquid elements from which it is produced; a very notable instance of this is acetylene (C2H2), hereafter referred to, whose combustion yields a much greater heat, and a correspondingly higher flame temperature, than is yielded by its constituents (C and H) when burned in their elementary, or uncombined, state.

The gasification of solid fuels in a central gas plant, and the distribution of the gas for divided uses, offer enormous advantage. In the case, for instance, of domestic appliances for burning solid fuels, the combustion of this fuel is, in general, imperfect, and probably exceedingly so; also, because of the slowness of putting solid fuel fires into and out of operation, and the difficulty of limiting combustion when heat is either not required or required only to small extent, produces a further very serious waste of fuel; in addition to this, the labor of handling the fuel and the ash and managing furnaces is great. On the other hand, in the central station gas works apparatus is operated continuously, and with maximum efficiency of heat consumption and minimum cost for labor; the gas is delivered to the consumer exactly when and in such quantity as he desires, and its consumption is begun and terminated instantaneously when required, its combustion is perfect, the heat is utilized with a maximum of efficiency, and the labor of controlling the gasconsuming appliance is almost nothing. The rapid advancement of the use of gas for domestic fuel testifies to this, and it is a probability of the future that the domestic gas-heating appliance will displace the coal-burning appliance, except possibly in cases of very large scale fuel consumption.

PROPERTIES OF THE INDIVIDUAL GASES CONSTITUTING, IN MIXTURE, THE INDUSTRIAL COMBUSTIBLE GASES.

The following table and appended notes give the essential properties of the various elementary combustible gases which, mixed in various proportions with each other and with incombustible diluting gases, constitute the various industrial combustible gases. The list of hydrocarbon gases and vapors is not complete—the number existing being very large—but those given are the ones of practical importance.

TABLE I.

		Weight	Heat of o	combustion U.'s.	Air required for combustion.		
Gas	Symbol	per cubic foot, lbs.	Per cubic foot.	Per pound.	Cubic foot of air. Per cubic foot.	Pounds of air. Per pound.	
Carbon (to CO) Carbon (to CO <sub>2</sub> ) Carbonic oxide Hydrogen	C C CO H <sub>2</sub>		323 326	4350 14544 4368 61523	2.393 2.393	5.771 11.541 2.471 34.624	
Hydrocarbon gases. Methane Ethane Ethylene Acetylene	CH <sub>4</sub> C <sub>2</sub> H <sub>6</sub> C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>2</sub>	.04234 .07940 .07410 .06880	1009 1764 1588 1477	23838 22226 21430 21465	9.570 16.748 14.355 11.963	17.312 16.156 14.836 13.313	
Hydrocarbon vapors Benzene. Toluene. Xylene. Naphthalene.	C <sub>6</sub> H <sub>6</sub> C <sub>7</sub> H <sub>8</sub> C <sub>8</sub> H <sub>10</sub> C <sub>10</sub> H <sub>8</sub>	.20640 .24345 .28050 .33870	3807 4552	18447 18699	35.888 43.065 50.243 57.420	13.313 13.547 13.720 12.984	

All weights per cubic foot are for the gases under 30 inches barometric pressure and at 60° F. temperature.

The product of perfect combustion of carbon is  $CO_2$ , and of hydrogen is  $H_2O$  vapor.

The weights per cubic foot of the products of combustion and their elements are as follows:  $CO_2$ , .1164 pound;  $H_2O$ 

vapor, .0476 pound; nitrogen, .0743 pound; oxygen, .0846 pound.

Dry air weighs .07658 pound per cubic foot; it consists of 20.9 per cent. oxygen and 79.1 per cent. nitrogen by volume, and of 23.13 per cent oxygen and 76.87 per cent nitrogen by weight.

The following is a brief statement of some additional facts concerning the foregoing individual gases, and their origin or formation, which are of importance in connection with our subject.

The combustible elements in all these gases are, of course, only two—carbon and hydrogen—the only ones available and recognized in practice as fuels. Carbon exists in combustible gaseous form in the hydrocarbons and also in CO, the product of its incomplete combustion with oxygen. Hydrogen exists in the hydrocarbons, and is also obtained, for the production of gas, by the decomposition of water.

## Hydrocarbons.

The hydrocarbons are of much importance. The luminosity of luminous gas flames is entirely due to them. Also, they contribute largely to the heating power of many gases; for instance (see analyses), ordinary carburetted water gas and coal gas derive more than one-half of their total heating power from them. They are, of course, the sole source of production of the pure oil gases.

The hydrocarbons are divided, it will be observed, into two groups—gases and vapors. The gases are not condensable at atmospheric pressure nor at any existing atmospheric temperature, and consequently each one is capable of being distributed and utilized, unmixed with other gases if desired, in the gaseous form. The vapors, however, at ordinary atmospheric temperatures have a pressure less—and, in the case of those of great molecular weight, very much less—than that of the atmosphere, and consequently would be condensed to the liquid form if subjected to atmospheric pressure; therefore, in order that they may be transported in their vaporous form they must be mixed with one or more of the permanent gases, which shall serve as a "carrier." It will be observed that the vapors have far the greatest weight of molecule and weight per cubic foot, their vapor pressure, which is a measure of their ability to retain the

vaporous form under pressure, in general decreasing as the weight of molecule increases. Both gases and vapors have, as shown by Table I, high heating power per cubic foot.

As to the natural sources and artificial methods of production of these hydrocarbon gases and vapors, the essential facts are these:

Certain of them are, or have been, formed by natural processes, and are thus available to us. The only instance of practical importance in connection with our subject, however, is natural gas, which is composed very largely, or almost entirely, of methane  $(CH_4)$ .

Certain of them are capable of artificial production or manufacture. The number which can be formed on a laboratory scale is large, and with the rapid development of synthetic chemistry practical processes will probably increase. A number of them are known to be produced in very small percentage directly from their elements, carbon and hydrogen, by the contact of these elements at high temperatures, which occurs, for instance, in the destructive distillation of coal in the coal gas processes, and in the manufacture of producer gas and water gas. Also, there exist some patented processes for the production of methane (CH<sub>4</sub>), on a commercial scale, from uncarburetted water gas, and by means of the catalytic action of nickel, etc., we are not aware that such artificial production of CH4 has yet been commercially effected, however. The one practically important case of artificial production of these hydrocarbons is acetylene  $(C_2H_2).$ 

The most important source of these hydrocarbon gases and vapors is their production, in the manufacture of artificial gas, from oil, the volatile portion of wood, and the volatile portion of bituminous coals, by the process of "destructive distillation." In this process the foregoing materials are subjected to the action of heat to either vaporize the liquid, in the case of oil, or volatilize the volatile portion of the material if a solid. If the materials are subjected to only a sufficient degree of heat to produce this vaporization, the distilled products will be, in great part, merely heavy vapors, and upon being subjected to atmospheric temperature and pressure will recondense to the liquid form, and they are, therefore, incapable of distribution as gas. These vapors are, therefore, after distillation subjected to a

still higher degree of heat. Under this treatment there is a chemical change produced. In this transformation there is, in general, a reduction of the molecular weight of the vapors, some free carbon being thrown down (lampblack or soot) and some free hydrogen liberated, and the resulting gas will be a mixture of free hydrogen, permanent hydrocarbon gases, and small percentages of various vapors which are carried by the permanent gases; this mixture is capable of distribution. If the degree of heat to which the original vapors are subjected in this process of destructive distillation were very high, they would be completely decomposed into their constituents, carbon and hydrogen; for the production of a gas of both good luminosity and good heating power, from oil or coal, the original distilled vapors are made to attain a temperature of about 1300° F. to 1400° F.

#### Carbon Monoxide.

When oxygen unites with carbon in combustion two products may, and in general will, be produced—carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>).  $CO_2$  is the product of complete combustion and is itself, of course, incombustible. Carbon monoxide is the product of incomplete or partial combustion, and is itself a combustible gas, as will be seen by the above table. The two reactions are as follows:

$$O_2 + C = CO_2$$
  
 $O_2 + 2C = 2CO$ 

The relative proportions in which CO and CO<sub>2</sub> will be formed are dependent upon the pressure and temperature at which combustion takes place and the length of time of contact of the air, and gases formed with the carbon; since in general gas manufacturing operations the pressure is sensibly that of the atmosphere, the temperature and time of contact are the controlling conditions. The quantity of CO produced will increase, and the quantity of CO<sub>2</sub> produced will consequently decrease. as the temperature is increased or velocity of flow decreased. Special experiments show that with exceedingly slow rate of flow, and a fuel (carbon) temperature of about 1900° F., practically only CO is formed; the CO<sub>2</sub> in the gas being only about one-half of 1 per cent.; with dry carbon and dry air supplied at 60° F., however, the heat of formation of the CO will be suffi-

cient to produce an actual temperature of off-going gas of about 2250° F., and a somewhat higher maximum temperature of fuel. (For further remarks on practical conditions see *Producer Gas*.)

Hydrogen.

July, 1913.]

As stated above, in gas manufacture hydrogen is produced from the decomposition of hydrocarbons. Another source fully as important is the decomposition of water vapor by its contact with a hot "reducing" agent. In the manufacture of combustion gases this reducing agent is, very generally, incandescent carbon (coal or coke). The oxygen taken from the water vapor and uniting with the carbon may, as shown in the above case of carbon monoxide production, form either carbon monoxide or carbon dioxide. All reactions are shown by the following formula:

$$H_2O + C = CO + H_2$$
  
 $2H_2O + C = CO_2 + 2H_2$ 

The percentage of the total steam supply which will be decomposed and the respective percentages of CO and CO<sub>2</sub> which will be formed are, as in the foregoing production of CO, dependent upon the pressure and the temperature at which the reaction takes place and the length of time of contact, the percentages of steam decomposed and of CO formed increasing with increasing temperature of reaction and time of contact.

In a quiescent state of steam and gas, or with so slow flow as to approximate this, special experiments show that a fuel bed temperature of 1900° F. is sufficient to decompose practically all the water vapor supplied and produce only the CO. In practical work the fuel bed is operated at a much higher temperature than this in order to permit the effecting of these chemical changes at the high velocities of steam and gas actually employed; also, in pure water gas manufacture (see "Water Gas" following) the heat necessary for these reactions must all be stored in the fire by preliminary heating. Owing to the velocity and gradual dilution of the steam, a very considerable percentage of it will remain undecomposed, and there will also be some CO<sub>2</sub> formed, even at the high temperatures employed in practical work.

It is scarcely necessary to call attention to the fact that, Vol. CLXXVI, No. 1051—2

since this decomposition of water vapor is the inverse of combustion of hydrogen, it is a heat-absorbing process. If, as is always the practical case, water vapor (steam) is supplied to the hot carbon, the heat required to liberate I pound of hydrogen (by decomposition of 9 pounds water vapor) will not be the 61,523 B.T.U.'s indicated by Table I, which figure includes the latent heat obtained in the condensation of the H<sub>2</sub>O vapor to the liquid form; it will be only about 52,000 B.T.U.'s. this figure and that for the heat of formation of CO in Table I. an easy calculation shows that (assuming only CO formed) for each I pound of water vapor actually decomposed, two-thirds of a pound of carbon is carried away from the fuel bed in the CO of the resulting gas. The decomposition of the I pound water vapor will absorb about 5780 B.T.U.'s, the combustion of the two-third pound carbon to CO will develop about 2000 B.T.U.'s, or there will be a net absorption, with consequent cooling effect, of about 2880 B.T.U.'s: to this cooling effect must be added the heat absorption necessary to raise the temperature of the total resulting gas (CO and H<sub>2</sub>) and any undecomposed steam to the temperature of its discharge from the fire, which will vary somewhat according to method of operation.

VARIOUS INDUSTRIAL GASES: THEIR QUALITIES AND MATERIALS EMPLOYED FOR MANUFACTURE OF ARTIFICIAL GASES.

In the following are given tables of analyses, which, with their appended text, give the kinds and volume percentages of the various foregoing elementary gases which, in simple mixture, constitute various industrial gases, the properties,—illuminating power, calorific power, flame temperature, etc.,—of these industrial gases, and their suitability for various uses; also, in the case of artificial gases, the materials from which they are produced.

The gases are good representatives of the products formed by the various methods outlined in remarks under Table I destructive distillation, imperfect combustion of carbon by air with the formation of CO, the decomposition of water vapor by carbon with liberation of free  $H_2$  and formation of CO, and combinations of these methods.

Notes.—In the case of the fuel analyses, the "proximate" analysis is obtained by drying the sample to drive off moisture,

then distilling to drive off volatile matter, then burning off the fixed carbon, successive weighings giving the various constituents; this analysis gives no information as to the quality of

TABLE II.

Typical Gas Making Materials.

Analysis No	I	2	3	4	5	6	
	Peat.	Lignite.	Bitumino	ous Coals.	Anthracite.	Oil.	
Proximate analysis.							
Moisture	35.0	35.0	1.3	.7	3.0		
Volatile matter	42.5	25.1	36.7	17.9	5.6		
Fixed carbon	19.0	34.7	53-5	75.8	80.5		
Ash	3.5	5.2	8.5	5.6	10.9		
Sulphur			1.7	1,2	.83		
Ultimate analysis.							
Carbon	53.0	69.5	77.6	84.	83.7	84.9	
Hydrogen	6.0	5.0	5.0	3.6	1.8	13.5	
Nitrogen	1.8	1.5	1.5	1.7	.7	.2	
Sulphur		1.5	1.7	1.2	.9	Trace	
Oxygen	34.0	17.0	5.7	3.8	1.7	1.4	
Ash	5.2	5.5	8.5	5.7	11.2		

TABLE III.

Gases Produced by Destructive Distillation.

Analysis No	7	8	9	10	II
	Peat gas.	Lignite gas.	Bituminous coal gas.	Oil	Gas.
Illuminants	6.0	3.0	3.8	.4	38.1
CO	17.0	18.2	8.7	5.0	•5
H <sub>2</sub>	27.0	44.I	50.5	78.9	3.4
CH4	19.0	15.4	28.2	11.0	57.7
C <sub>2</sub> H <sub>6</sub>			2.8		
$\mathbb{C}O_2$	27.0	13.0	2.I	I.I	
02	1.0	1.3	•4	.6	
N <sub>2</sub>	3.0	5.0	3.5	3.0	•3
Candle power			13.0	none	60.
Calorific power B.T.U.'s	467.8	424.	610.	394.	1488.
Specific gravity	.826	.596	.428	.222	.881

TABLE IV. Various Gases.

Analysis No.	I 2	13	14	15	16	
	Water gas.		Producer gas.			
	Uncarbur- etted.	Carbur- etted.	Anthra- cite.	Bitumi- nous.	Natural Gas.	
Illuminants		10.7			.1	
<u>C</u> 0	43.5	33.4	25.0	22.0	.2	
$H_2$	47.3	38.1	14.2	10.5		
СН4	.7	7.6	•5	2.6	97.1	
C2H6		2.4		.6		
CO <sub>2</sub>	3-5	3.3	6.3	5.7		
O <sub>2</sub>	.6	.7	.I	.4	.5	
N <sub>2</sub>	4.4	3.8	53.9	58.2	2.I	
Candle power	none	20.2	none	none	5.0	
Calorific power B. T. U.'s	302.	602.	132.	132.	982.7	
Specific gravity	-559	.676	.871	.889	.566	

the volatile matter. The ultimate analysis gives accurately the chemical composition; the ultimate analysis is, of course, of a dry sample.

In the case of peat and lignite their respective proximate and ultimate analyses (Analyses I and 2) and the analyses of the gases yielded (Analyses 7 and 8) do not relate to identical samples of these materials, such simultaneous data not being readily accessible to the writer; they are all correct, actual analyses, however, and accurately represent the facts intended to be brought out; the sample of lignite yielding the ultimate analysis shown is of rather unusually good grade.

The bituminous coals (Analyses 3 and 4) will generally, on being heated and before giving off their volatile matter, "cake"

or melt, and assume a plastic form.

Coke, which is now greatly replacing anthracite, has, in general, even more fixed carbon and less volatile matter than anthracite.

In the gas analyses, under "illuminants," are grouped several different hydrocarbons, chiefly ethylene  $(C_2H_4)$ , which, as the name indicates, impart luminosity to the gas flame; this group will vary slightly, in different gases, in constituency and calorific power per cubic foot; this calorific power will generally be somewhere about 2250 B.T.U.'s per cubic foot.

The distillation gases shown, produced from peat and lignite, are not commonly manufactured; neither is the light oil gas (Analysis No. 10), this being a sample of a gas made for balloon inflation, and which was required to be very light; these analyses are introduced simply for illustration of principles elsewhere mentioned.

The following is a brief statement of the qualities necessary in gases for various uses, and the suitability of the respective foregoing gases for these uses.

## Flame Temperature.

In cases where low temperature work is to be done, high flame temperature is, of course, not so essential to efficiency of utilization of heat. In other cases, however,—as, for instance, in the use of gas for illuminating by the Welsbach mantle, the melting of refractory metals, etc.,—where the effect desired is obtained only at a high temperature, a very hot flame, or products of combustion, is very necessary for efficiency in utilization of heat, since it is only the excess of temperature of the flame above the physically or chemically necessary point which

accomplishes any useful work. Recuperation, or heating of air and gas before combustion by the heat of the waste products of combustion, can in many cases be practised, and thereby increase the efficiency of a low flame temperature gas, but in many other cases, as in the use of gas for illumination or other purposes, where gas is divided and used in small individual quantities, it is impracticable; the gas and air supply must be cold, and consequently the gas must be capable of yielding high flame temperature under this condition.

If a flame be protected from any loss of heat by radiation or conduction the products must carry away all the heat generated, and consequently the quantity of heat generated divided by the quantity of heat necessary to raise the products of combustion one degree in temperature will give the rise of temperature; adding to this the temperature of the gas and air before combustion will give the final flame temperature. This flame temperature can be approximately calculated; it cannot be accurately calculated, however, for, although heats of combustion of elements and gases have been accurately experimentally determined, the heat required to raise the temperature of the products of combustion one degree ("specific heat") has not, though approximately correct information has been obtained.

Even if we possessed the correct foregoing data for the calculation of flame temperature, however, that which exists in practice would be less for the following reasons. There is unavoidable some loss of heat from a flame, while combustion is in progress, by radiation and conduction. It is impracticable to obtain the ideal proportions of air and gas in combustion. There is also undoubtedly delayed combustion; in very hot flames the temperature of dissociation of a portion of the products of combustion is reached, and the combustion will consequently not be completed until some heat is dissipated.

Below are given the flame temperatures of certain gases, some determined by direct experiment and others calculated. The following remarks are made concerning them.

The experimental figures are quoted from a very good authority who made these determinations. They were made by a method which avoided the necessity of introducing any pyrometric device into the flame, with consequent lowering of temperature. Although they are commented upon by another

authority as being possibly somewhat high, they probably represent nearly the correct facts. As somewhat of a check upon them, it may be remarked that even with a small Bunsen burner of good design, consuming ordinary illuminating gas, it is possible to fuse platinum; as this temperature appears pretty positively determined to be over 3200° F., and as there is also in such case necessarily the loss of some heat from the flame by conduction, etc., it seems that in a large flame burned under the best conditions it should be possible to attain somewhere about

the 3400° given by this experimenter.

The calculated temperatures have been computed by the writer; they are, as might be expected for reasons given in the foregoing, higher than the experimental figures. As to the important matter of specific heats to be used in making these calculations, from the writer's information there appears to be pretty close agreement among authorities in the case of nitrogen. carbon monoxide and carbon dioxide. In the case of water vapor we believe there is not such close agreement; the figures quoted seem to represent best information until at least recent date, though still more recent determinations seem to indicate that the quoted figures are too high. This last, if correct, would, of course, mean that the calculated temperatures for combustible containing hydrogen are too low. In connection with this, note that the calculated and experimental temperatures of hydrogen agree rather more nearly than is to be expected, though this may indicate either that the calculated temperature is too low, or else that the actual combustion of hydrogen is so efficient as to develop more nearly the theoretical temperature than in the case of carbon. The following are the specific heats assumed by the writer in making these calculations. (These specific heats are, of course, for constant pressure, which applies in the case of flames at atmospheric pressure; at constant volume,—as in the case of gas burned in a confined space,—the specific heat will be much lower, and consequently tend to give higher temperature of products of combustion);—

SPECIFIC HEATS AT VARIOUS TEMPERATURES FAHRENHEIT.

	2200°		0	3300°	0
Carbon monoxide (CO) Nitrogen (N <sub>2</sub> ). Carbon dioxide (CO <sub>2</sub> ). Water vapor (H <sub>2</sub> O).	.2920	.3040	.3112	.3184	.3256 .3676

FLAME TEMPERATURES.

Substance.		Temperature ° F. Experi- Calculated mental.	
Carbon to CO2.	Air		3540
Carbon to CO	Air		2260
CO to CO <sub>2</sub>	Air		3670
Hydrogen	Air	3450	3510
Hydrogen	Oxygen	4400	
Illuminating gas	Air	3400	
Illuminating gas	Oxygen	4000	
Acetylene	_ Air	4600	
Acetylene	Oxygen	7200	
Producer gas (Analysis No. 14)	Air		2735

In order that the foregoing may have some practical significance, the following few temperatures required in certain common high temperature industrial operations are quoted from various authorities;—

TEMPERATURE AT VARIOUS POINTS OF MANTLE OF WELSBACH LAMP.

			Degree	es Fahr	enhei
Ordinar	y lam	p	2200	to	2650
"High	pressu	re" (high gas consumption) lamp	2400	to	2850
Melting	-point	of cast irons	2000	to	2500
"		wrought irons	2700	to	2900
4.4	4.4	steels		to	2700
44	6.4	nickel		3000	
4.4	4.6	platinum		3227	
6.6	4.6	quartz		1000 -	-

The foregoing figures indicate that hydrogen, carbon monoxide and the hydrocarbons are all capable of giving very high flame temperatures, and that consequently the gases of Tables 3 and 4 (coal gas, carburetted and uncarburetted water gas, the oil gases, etc.) which are composed of them, and this with little dilution by incombustible gases, are all suitable for high temperature operations. Producer gas, on the other hand, owing to the presence of large quantities of incombustible nitrogen and carbon dioxide, gives far lower temperature.

A point in connection with this subject which is worthy of a moment's notice is the following. In Table I are given the actual heats of combustion of the various hydrocarbons, which hydrocarbons enter into the composition of some of the commercial gases given in Tables III and IV. If we calculate the heats of combustion of the elements (carbon and hydrogen) contained in these hydrocarbons, and compare them with the actual heats of combustion of the hydrocarbons themselves as given in Table

I, the two will be found to not agree, and this is for the following reasons. As is the case in all chemical combination, heat is evolved in the union of the carbon and hydrogen to produce these hydrocarbons, and, of course, the molecule will correspondingly resist decomposition into its elements, which decomposition must take place before combustion can occur: this heat absorption in decomposition will, therefore, affect the heat of combustion as compared with the calculated heat of combustion of the constituent carbon and hydrogen, as just stated. Methane (CH<sub>4</sub>) has the highest heat of formation of the hydrocarbons which we are considering; its heat of combustion per cubic foot is (Table I) 1009 B.T.U.'s, whereas that of its constituent carbon and hydrogen is just about 100 B.T.U.'s greater; its flame temperature, therefore, must be somewhat lower than that of its elements. This heat of formation of hydrocarbons is in general low, however. Indeed, in a number it becomes apparently negative, which means that the work of decomposing these hydrocarbons for combustion is less than that which would be required in decomposing the elements (carbon and hydrogen) in their elementary condition. A very notable and practically important instance of this is acetylene (C<sub>2</sub>H<sub>2</sub>). The heat of combustion of one cubic foot of this gas is, from Table I, about 1477 B.T.U.'s, whereas the sum of the heats of combustion of the two constituents, carbon and hydrogen, is only 1250 B.T.U.'s; since the products of combustion from the elements and the gas are identical, the flame temperature of the gas must be much the higher. This fact accounts for the very high flame temperature of acetylene shown above, which contributes to its very high illuminating power, and renders the gas valuable for certain practical uses, such as the cutting of metals, etc. In connection with this peculiarity, it may be remarked that acetylene is, primarily, a high temperature product, the calcium carbide from which acetylene is generated, being itself formed only at the exceedingly high temperature of the electric arc, and there is, therefore, primarily the expenditure of very considerable energy to effect the ultimate forcing of carbon and hydrogen into this combination. Acetylene is the only hydrocarbon which exhibits this negative heat of formation, or endothermic property, in marked degree, and it is not a component of any

of the commercial gases shown in Tables III and IV in any measurable quantity.

## Luminosity.

In former times light was obtained from only those gases giving luminous flames; although this method of obtaining light from gas is still employed, it becoming largely displaced by the use of the Welsbach mantle. As is stated in the remarks under Table I, the luminosity of gas flames is due to the presence in the gas of hydrocarbons, and these hydrocarbons are generally obtained only from high-grade bituminous coals and oil; consequently, for the furnishing of a luminous flame gas we are considerably restricted in our choice of materials and also methods of manufacture, which must necessarily mean increased cost of gas manufacture. With the Welsbach light, on the other hand, it is only required that the gas shall furnish a high temperature flame, and, as is shown in the above remarks on flame temperature, it is easy to manufacture from a very wide range of fuels gases (for instance, uncarburetted water gas, or a feebly luminous mixture of uncarburetted water gas and coal gas, or a low-grade coal gas) which shall have such abundantly high flame temperature. Hydrocarbons in a gas, as is above shown, do not necessarily increase the flame temperature, and those existing in the bulk of the industrial gases are of no more value for the production of heat or flame temperature than is carbon in the fixed form in all of the fuels from which can be readily produced the foregoing satisfactory gases. Furthermore, the quantity of heat required to furnish a given quantity of illumination is vastly less with the Welsbach mantle than with the luminous flame; one candle hour can be obtained with the Welsbach light with a consumption of from 36 B.T.U.'s with the ordinary low-pressure light to 20 B.T.U.'s with special, but now very commonly used, high-pressure lights; with the luminous flame. and using the good grade of coal gas shown in Analysis No. 9 of Table III, 235 B.T.U.'s will be required to furnish one candle hour. Incidentally, it may be mentioned that, while these hydrocarbons thus have in general practical cases no especial value as heating agents, many of them are of much value for chemical purposes and can, with profit, be extracted from gas and applied to these more valuable uses.

The foregoing facts are tending, and very properly, to lessen the legal requirements imposed with respect to luminous flame qualities of commercial gas, and this movement is certain to continue.

# Calorific Power and Weight.

From the above it will be seen that the calorific power of a gas per cubic foot does not necessarily affect flame temperature (compare uncarburetted water gas, coal gas, and rich oil gasall high flame temperature gases), and is, therefore, not of importance with respect to the heat efficiency of the gas when consumed. In the matter of distribution of gas, however, where expensive pipes and appurtenances and pumping machinery must be employed, this calorific power, and also the weight or specific gravity of the gas, have an influence which merits a moment's attention. Consider, for example, the transportation and distribution of a given quantity of energy per hour in two gases which could be produced from bituminous coal, one being producer gas, the other being a mixture of coal gas distilled from this coal, and the uncarburetted water gas which can be made from its residual coke. Approximately, these gases would have, respectively, calorific powers as 1 to 3 and specific gravities as 2 to I. It is evident that the quantity to be transported of the first gas is at least three times that of the second, which will require pumping machinery of three times the capacity. (from the law of flow of gas through pipes), with identical pressure conditions in pipes, the first gas would, because of its three-fold volume and greater specific gravity, require pipe capacity (sectional area) about four times that required for the second gas, and would require mechanical work by pumping machinery more than three times that required for the second gas; or, with identical pipe capacity, the pressures for the first gas must be much higher, and the mechanical work of compression many times as great as for the second gas. In long-distance transmission of gas, where the initial pressure would be some, or many, atmospheres, this work of mechanical compression is an item of importance.

The foregoing striking example is chosen simply for illustration. Naturally, the manufacture of such a gas as this producer gas for long-distance distribution would not be attempted.

#### MANUFACTURE OF ARTIFICIAL GASES.

In the following is given a brief description of the methods of manufacture of the various artificial gases shown in Tables III and IV, and the general theoretical principles underlying these methods: also illustrations of representative forms of apparatus for the production of each of these gases.

#### Coal Gas.

July, 1913.]

This gas forms a very large portion of the entire commercial supply of combustible gases, especially those distributed for sale and use for illumination and other domestic purposes. "Coal gas" proper is the product of destructive distillation of bituminous coals which contain "volatile combustible," or matter—chiefly hydrocarbons—which can be driven off in the form of vapor, and permanent gas, by the simple application of heat. Other solid fuels shown—wood, peat, lignite—contain such volatile combustible in greater or less amount, and can be similarly treated, yielding a somewhat similar combustible gas, though, as shown by the analysis, the quality of gas produced is very dependent on the kind of material used, the "volatile combustible" differing greatly in quality in the various materials.

Let us briefly consider the materials, since they affect the quality of gas produced. In the formation by the processes of nature of high-grade coals from the original vegetable substances from which they are produced, there is a continual change of chemical constituency, as will be seen by comparing the analyses, beginning with peat and terminating with anthracite coal. The most important is the gradual elimination of oxygen, this existing in high percentage in peat, lignite, etc., and practically disappearing in anthracite coal. Also, hydrogen similarly decreases, though much more slowly; it remains in slightly diminished percentage in the hydrocarbons of the high volatile bituminous coals, but it is present in only small amount in anthracite coal.

The effect of the constituency of the material which is used upon the gas produced will be seen by comparison of the various gases,—those from peat, lignite, and bituminous coal (see Analyses 7, 8, and 9). The chief difference in quality of these gases is caused by the different quantities of the oxygen content of the respective materials. At the temperature of distillation and gasi-

fication this oxygen unites with part of the carbon in the fuel to form CO and CO<sub>2</sub>, the latter being formed in very heavy quantity and passing off with the gas produced. This dilutes the combustible gases, and being itself incombustible it lowers the heating power and flame temperature of the gas; also, it very seriously injures the luminous qualities of the gas. The removal of the CO<sub>2</sub> by purification processes would be expensive; it may be removed by passing the gas through incandescent carbon, but this will result in a destruction of the hydrocarbons. Furthermore, it will be observed that the low-grade materials contain a large percentage of moisture, which will even remain in very considerable quantity after the most thorough drying practically possible; this is objectionable in the process of distillation. Also, the coke formed is generally in very poor quality. facts prevent the use of these low-grade materials for coal gas production; the material generally employed is a high-grade, high volatile bituminous coal, such as shown in Analysis No. 3.

In the practical distillation or "carbonization" of gas coal this coal is enclosed, in masses ("charges") of very considerable volume, in some form of retort, and the exterior of the retort subjected to heat. To obtain rapid work and thus effect economy of carbonizing plant, the temperature of the exterior of the retort is made much higher than the temperature required to be attained by the material and the vapors for the distillation and gasification: the exterior of these retorts will ordinarily be from 2200° to 2600° F., or even slightly higher, whereas, as earlier stated, the best temperature to be attained by the distilled vapors for gasification is 1300° F., or slightly higher. It is evident that the heat necessary for the distillation of the interior of the "charge" must be transmitted through the exterior of the charge, and the gases evolved from the interior must, at least in part, and to an extent depending upon the form of retort, pass off through the exterior. Therefore, before the distillation in the interior can be completed, the exterior of the charge and the retort adjacent to it will have attained a very high temperature, and in the passage of the vapors and gas through this heated exterior there is some destruction of hydrocarbons, with consequent lowering of heating power and luminosity of the gas produced. Analysis No. o represents, however, the average quality of the gas produced during the distillation of an entire charge; the gas at the beginning of the distillation period will be very much richer, and that at the end very much poorer, than this average. It is, furthermore, evident that even the lower grade coal shown in Analysis No. 4 may be capable of yielding, in the early portion of its carbonizing period, a gas of as good quality as that shown in Analysis No. 9; the average gas produced during the entire carbonizing period would, however, be of poorer quality.

Although not a subject for detailed consideration herein, a few words may be added concerning the other substances,—residuals or by-products and impurities,—formed in the manufacture of coal gas. The chief such substances and their deri-

vation are the following:

The carbon of the bituminous coal which is not capable of being driven off in gaseous or vaporized form remains in the retort, after the distillation is completed, as coke. The proximate analysis of fuel (see Table II) is obtained by the distillation of only a small sample of coal, and, furthermore, this distillation is performed rapidly; these conditions cause the volatilization of a greater percentage of weight of the coal than is obtained in the slower distillation of very large masses of the coal in practical work. Hence, referring to Analysis No. 3 of Table II, although the proximate analysis indicates that the vield of coke should be 62 per cent. (fixed carbon plus ash) of the weight of the coal, the coke remaining in actual practical work would be about 68 per cent.; this is caused in greater part by the filtering out and decomposition of tars and heavy vapors in the large masses of coal treated, and at the temperatures employed, in practical work, the free carbon thus thrown down adding to the volume of the coke; also, the volatile matter will not be quite completely expelled from the coal in practice. The quality of the coke will vary according to the coal used and the method of carbonization. Even with coals of about the same grade in other respects there may be very considerable difference in coking quality, and differences in fineness or freshness from the mine also have an effect; the density and firmness of coke will in general increase with increase in internal pressure in the charge of coal and the length of time of carbonization.

Of the total nitrogen contained in the coal, as shown in the analysis, a portion will remain in the coke after distillation. The remainder, driven off with the gas, is in great part in the form

of ammonia  $(NH_3)$ , either in the free condition or combined with sulphur compounds and  $CO_2$ . It is recovered by proper methods (the free  $NH_3$  is easily recovered, for instance, by simple absorption in water, I volume of water at  $60^{\circ}$  F. absorbing about 780 volumes ammonia) and sold, being a very valuable by-product. A portion of the nitrogen coming off in the gas is in the uncombined form. A small further portion of the nitrogen unites with carbon to form cyanogen and its compounds; these compounds, which are used in, for instance, the manufacture of Prussian blue, are in large works recovered and form a by-product of some value.

Of the sulphur contained in the original coal a very considerable proportion remains in the coke. The remainder is driven off in the gas in the form of various compounds. The chief of these compounds are sulphuretted hydrogen  $(H_2S)$  and carbon bisulphide  $(CS_2)$ . The  $H_2S$  is formed in vastly the greater amount, and, to prevent the contamination of the combustion products of the gas when burned, it must be removed from the gas before distribution and use; this is generally done by passing the crude gas through hydrated oxide of iron. The  $CS_2$  is not thus easily removed; a small portion is removed in the foregoing passage through oxide, and, as the total quantity formed from a coal reasonably free from sulphur is small, the remainder is permitted to remain in the gas.

As has been before stated, a very considerable proportion of the hydrocarbon vapors distilled from the coal are of such heavy nature and of such slight degree of volatility that they cannot all be carried by the permanent gases. These heavy vapors are thrown down from the gas as soon as it cools to atmospheric temperature, after leaving the generating apparatus, and form tar.

The quantities of gas and the by-products, which will be obtained from one ton (2000 pounds) of coal of the quality shown in Analysis No. 3, Table II, will be, in good practice, as follows; though these individual figures will vary somewhat according to apparatus and other conditions:

Gas	10,500 cubic feet
Total coke	1300 to 1350 pounds
Ammonia	5 pounds
Tar	12 gallons
Candle power (flat flame)	13.

The quantity of fuel consumed in the carbonization of coal will, in present general coal gas works practice, be about 300 pounds per 2000 pounds of coal carbonized, depending on kind of apparatus and other conditions. The heat from this fuel will pass away from the apparatus in various ways, and the respective percentages dissipated through these various channels will evidently vary according to the form of apparatus and its operation. Some experiments have been made to ascertain the division of this total heat expended; one such experiment made, with much care, gave the following results. The form of apparatus used in this case was the horizontal retort setting described hereafter; it was provided with external recuperators, which probably somewhat increased the quantity of heat lost by radiation.

	Per cent.
In waste chimney gases (1112 ° F.)	25.2
In sensible heat of coal gas (1202 ° F.)	13.8
In sensible heat of coke (1742 ° F.)	18.5
Radiation, etc	20.7
Latent heat of formation of gas, etc	210
Heat of discarded ash	o 8
F.	
	100.0

It is of interest to note that this experimenter, and others, have carefully calculated from the analyses of the coal, and the gas and other compounds distilled therefrom, the quantity of heat required for the mere distillation of the volatile portion of the coal, and also the quantity of heat which is developed by internal reactions, during this distillation. While the different figures do not exactly agree, they all indicate that the net external supply of heat required is very small, or, in other words, the internal reactions generate quite, or very nearly, enough heat for this distillation. In the above itemized statement of heat losses is included the heat required for this distillation (latent heat of formation of gas, etc.), but this quantity of heat has already been charged into the gross quantity of heat supplied on which these percentages are based. The heat which requires to be supplied by the consumption of fuel is, therefore, apparently that represented by the above items of chimney gas waste, sensible heat of the offgoing coal gas, sensible heat of the hot coke as discharged from the retorts, radiation, and heat contained in the discarded ash.

The following illustrations and notes describe very good specimens of the various types of coal gas generating apparatus

used in practice.

The illustration below represents in elementary, but quite complete, outline the apparatus employed for the distillation of coal gas from coal, and its subsequent treatment to prepare it for distribution. The raw coal is placed in the closed externally heated fireclay retorts, and the coal gas is distilled. The exhauster mechanically draws the gas from the retorts in order to preserve the pressure within the retorts at, or very close to, atmospheric pressure, and thus prevent possible leakage of gas. The tar extractor removes the heaviest tar and oil, which is precipitated immediately on the issuing of the gas from the retorts.

COAL GAS APPARATUS

EXHAUSTER CONDENSER SCRUBBER PURIFIER METER HOLDER

Fig. 1.

The condenser provides for further cooling and condensation of oils into suspended drops. The washbox removes these oils. The vertical scrubber and the rotary scrubber together effect the removal of ammonia from the gas; this is done by subjecting the gas to thorough and lengthy contact with water at proper temperature, which absorbs the ammonia. The purifier removes the sulphur impurities—chiefly sulphuretted hydrogen (H<sub>2</sub>S)—from the gas; as has been before stated, the material commonly used for this purpose is hydrated oxide of iron, through layers of which the gas is slowly passed, the sulphur compounds being decomposed and the sulphur retained in the oxide. There are other chemical reactions, to more limited extent, in these various vessels. The gas is then measured in the meter, stored in the holder, and thereafter delivered through the governor, which

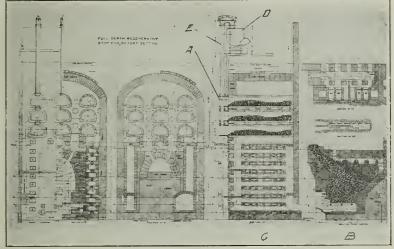
regulates pressure, to the street mains. In large works there is frequently very considerable auxiliary apparatus designed for the recovery of small percentages of by-products, such as cyanogen, and the manufacture of various individual products from the oils, tars, and ammonia; the apparatus shown, however, represents the essential processes of manufacture of the gas.

The further illustrations given will be only those of various forms of retorts for the distillation of the gas. It is these retorts and settings which chiefly vary in coal gas manufacture,

Fig. 2.



July, 1913.]



Stop-end horizontal coal gas retorts and setting.

and which are, therefore, of special interest to us; the treatment of the gas after distillation will be practically the same, whatever the form of retorts employed.

The above illustration shows—though not all assembled as in actual construction (this assembling being shown in the next illustration)—the various parts of a setting of "stop-end" horizontal retorts such as are used in coal gas works. This form, though of very much cruder construction, is that which was used in the earliest manufacture of coal gas; in the improved form here shown and with greatly improved appurtenances, they are still in very extensive use.

Vol. CLXXVI, No. 1051-3

The retorts (A) as shown are permanently closed at one end, and consequently the coal must be introduced into, and the coke withdrawn from, the same end of the retort; formerly this work was performed by hand, with shovel and rake, but modern plants are equipped with very complete and satisfactory machinery for the much cheaper mechanical execution of this work.

In the furnace, or "producer" (B), is consumed the solid fuel (coke) used for heating the retorts; for reasons given in later remarks on producer gas, a small quantity of steam, or

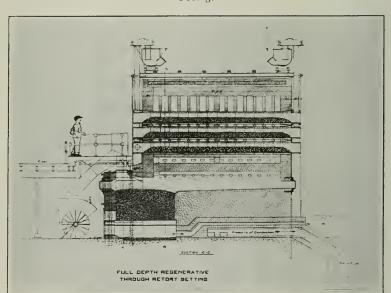


FIG. 3.

Through horizontal coal gas retorts and setting.

products of combustion, is generally admitted with the air supply to this fuel bed to prevent excessive temperature, and consequent trouble from clinker. Hot combustible producer gas issues from the top of this fuel bed, which is led in a number of divided streams into the arched space enclosing the retorts, is there mixed with a supply of secondary air, and burned for the heating of the retorts. Recuperators (C) are provided containing contiguous ducts for, respectively, the hot waste gases which have heated the retorts and the incoming air for combustion;

the air and hot waste gases have counterflow, and the sensible heat of the waste gases is, in great part, imparted to, and preheats, the air. In general present practice it is only the secondary air, or that which is to be supplied to the retort chamber for the combustion of the producer gas, which is heated, the preheating of the primary air for supply to the fuel bed having objectionable features.

The distilled gas, after issuing from the retorts, is carried into the "hydraulic main" (D) by the "standpipe" (E), the end of which pipe is lightly sealed in liquor in the hydraulic main; this prevents the return of gas from the gas mains back into the retort when the latter must be opened for charging or

discharging.

The material employed for the construction of these retorts, their combustion chambers, recuperators, and setting, is fire-brick. Furthermore, to avoid melting or distortion of these parts under the high temperatures employed and the breakage of retorts, this fire-brick must be very refractory to heat, strong, and the most careful attention must be given to its proper burning before installation.

Fig. 3 shows a complete section of another form of horizontal retort and setting—the "through" retort. This form is

coming into extensive modern use.

As is seen, this retort has a removable door at each end. This permits greater freedom in charging and discharging operations; instead of the coke being raked out of the same end of the retort at which is stationed the coke-removing device, a ram can be introduced into one end of the retort and the coke pushed out from the other end. It is also possible by this "through" construction of retort to charge the retort more fully with coal than is the case with the "stop-end" form; in the latter, space must be left for the insertion of the coke-drawing device, which is not necessary where the coke is pushed from the "through" retort. This more complete filling of the retort leaves less free space, and consequently hastens the exit of gas, which gives less liability to decomposition of hydrocarbons and also ammonia.

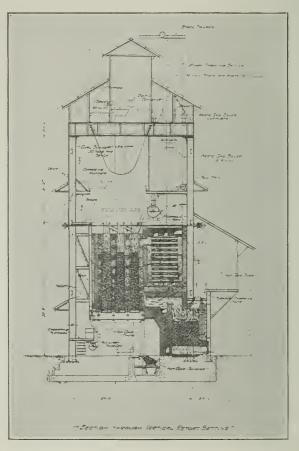
As shown, this form of retort is provided with a "standpipe" for the removal of gas at each end of the retort.

Observe the arrangement for dropping hot coke from the retort directly into the producer.

This setting is, of course, provided with recuperators for the preheating of air by the waste combustion gases, the same as shown in the above "stop-end" retort setting.

In modern construction these retorts are 21 feet long, contain a maximum charge of 1400 pounds of coal, and the length

FIG. 4.



Vertical retorts and setting. The United Gas Improvement Co.

of time for distillation or carbonizing of such charge is about seven hours.

The above illustration shows a setting of vertical retorts. Although retorts of such vertical form have for many years been employed for the distillation of an oil-containing rock, or

"shale," it is only within recent years that it has been employed for the distillation of coal and production of coal gas.

The advantage of this form of retort is that it permits charging of coal and discharging of coke by gravity, thus greatly lessening the labor cost for these operations which exists in horizontal form of retorts. Another advantage is that the plant occupies much less ground area for a given capacity than is the case with horizontals. Also, because of the greater depth of the charge of coal and the slower distillation, the coke produced is of excellent quality—dense, firm and suitable for metallurgical operations—and also contains less fine material, or "breeze," which is of much less value than the larger coke.

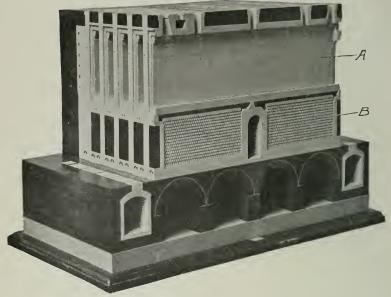
A noteworthy feature of this form of retort, as compared with the horizontal forms above shown, is that the entire cross-section of the retort is filled with coal. This leaves no, or very little, free space between the coal and sides of the retort. Consequently, gas is distilled at the surface of the coal and, in great part, flows inward toward the cooler interior of the charge, rises through it to the top of the retort, and is discharged. There is, therefore, less danger than in the horizontal form of decomposing of the hydrocarbons of the gas by contact with the very hot sides of the retort. Indeed, in this particular system an empty heated space, as shown, is left above the top of the charge of coal, through which the gas flows slowly and is subjected to additional heat for its more complete gasification.

The gravity charging and discharging feature of vertical retorts makes possible continuous charging and discharging, fresh coal being continuously fed to the top of the retort and coke continuously withdrawn from its bottom; such continuous retorts are now in practical use, though as yet to limited extent. The retort shown in our illustration, however, is not thus continuously acting, the entire retort being charged with coal, and emptied of coke, at fixed intervals.

In most recent construction these retorts are about 18 feet in length, and receive from 1000 to 1700 pounds of coal per charge. The time required for the distillation, or "carbonization," of this charge is from nine to twelve hours. The empty space above the coal is about 4 feet in length.

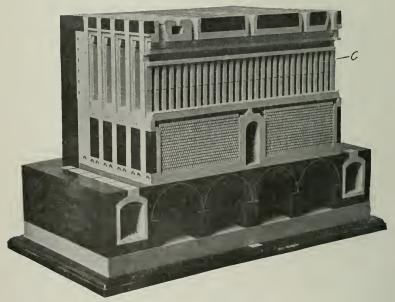
This form of retort furnishes not only, as above stated, an excellent grade of coke, but also an excellent quality and large quantity of gas.

FIG. 5.



Kopper coke oven.

Fig. 6.



Kopper coke oven.

The desire for coke-producing apparatus which should be more economical in respect to recovery of the by-products—gas, ammonia, tar, etc.—than the old bee-hive oven has led to the development and the very extensive modern use of the "by-product" coke oven. The gas produced from these ovens is becoming increasingly important for use in industrial purposes, and even in part for distribution, for general public use, by gas companies.

These ovens are designed primarily for the production of a superior grade of coke suitable for metallurgical purposes, etc. Consequently, the grade of coal chosen for use and the method of operation are generally such as to produce this best grade of coke; the gas is a by-product and is a secondary consideration. In many cases only the richest portion of the gas, which is that given off during the earlier portion of the carbonizing period, is sold for public supply, the remainder of the gas being used for the heating of the retorts. It is possible, however, with a good grade of coal and careful operation, to produce a total gas of very fair quality.

These ovens are generally installed in very large capacity, and require heavy machinery and appurtenances. They are not generally suitable for the use of moderate-sized gas works for the production of coal gas; furthermore, the quality of gas is not under such thorough control as in the above-described smaller forms of retort, and is in general somewhat inferior. For gas works use the above-described horizontal or vertical form of retort is preferable.

Figs. 5 and 6 represent models of one of the most modern by-product ovens. These models do not show the hydraulic mains, piping and machinery required for operation; they show very clearly, however, the construction of the retorts themselves, and as these are the things of chief interest to us these views are very satisfactory. An illustration of a complete oven, though of different design, is shown below.

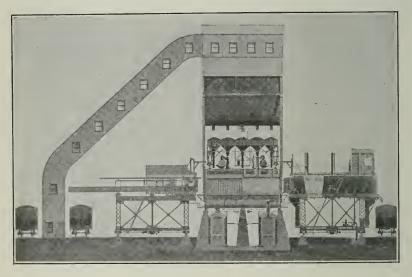
The first view shows a section through the retort proper (A) and through the fire-brick recuperators (B); the second view shows a section through the flues (C) contiguous to the walls of the retorts, which carry the hot gases which heat the retorts.

The fresh coal is charged, by gravity, through the openings shown at the top of the retorts. The coke remaining after

carbonization is pushed out horizontally by a powerful ram, there being sealed doors at the ends of the retort which are opened for this purpose.

In modern construction these retorts are 18½ to 21 inches (taper) wide, 11 feet high, and 39 feet long, and contain a charge of about 13 tons of coal; this large scale handling of materials is, of course, favorable to economy of labor. The length of time required for distilling or "carbonizing" a charge is with this size of retort from eighteen to thirty hours.

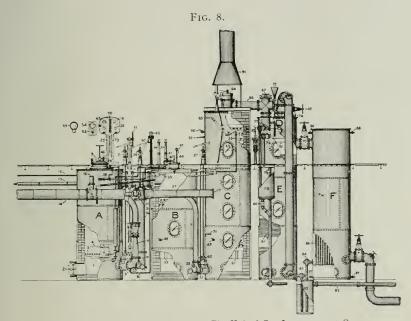
Fig 7.



United-Otto system coke oven.

By-product oven retorts are generally provided with two gas exits and sets of piping; this permits the separate withdrawal, if desired, of the rich gas at the beginning of distillation and the poorer gas at the close of the distillation. As above stated, the poorer gas is frequently used for the heating of the retorts; where it is desired to otherwise dispose of this gas, however, these ovens are provided with producers for the combustion of solid fuel, as in the case of the above-described horizontal and vertical coal gas retorts, and the heating of the retorts is done by this producer gas.

Fig. 7 shows a complete installation of these coke ovens, though of somewhat different design from the models shown in the previous illustrations. Little explanation of this construction is required. On the left is the coal elevator delivering coal from the railway car to the storage bin above the retorts, whence it is fed into the charging hoppers and thence into the



Carburetted water gas apparatus. The United Gas Improvement Co.

retorts. Beneath the retorts are shown the checker-brick filled recuperators, which absorb the sensible heat of the waste products of combustion, and return this heat to the incoming air supply for combustion. On the left is seen the movable structure carrying the ram which pushes the coke from the retorts; this coke is received and cooled on the movable platform at the right, and thence discharged into cars.

# Water Gas-Uncarburetted and Carburetted.

The above illustration shows a standard form of apparatus for the manufacture of carburetted luminous flame water gas. Since, in this process, one part of the operation is the production

of uncarburetted, or plain "blue," water gas, the production of both kinds can be considered together.

The generating apparatus proper consists of three steel shells, called, respectively, the generator (A), carburetter (B), and superheater (C), all lined with fire-brick, and the carburetter and superheater filled with fire-brick laid in "checker" form so as to be easily traversable by gases. The generator contains a bed of fuel—anthracite coal or coke—of, generally, from 5 to 7 feet in depth. (The succeeding vessels—scrubber and condenser—are simply for the cooling of the gas and the extraction of tars, etc.)

The operation of this apparatus is intermittent, or in cycles, consisting of two parts—first, the heating operation or "blow," and, second, the gas-making operation or "run." Briefly, the description of these operations is as follows:

In the blow, forced blast is supplied to the fuel bed for its heating. As stated in remarks under Table I (see also remarks hereafter on producer gas), the combustion gases issuing from the top of the fuel bed will contain both CO<sub>2</sub> and CO, the latter continually increasing in percentage as the temperature of the fuel bed rises during the blow. These combustion gases are led to the top of the second vessel, the carburetter, and here a secondary supply of air is admitted for the combustion of the CO. The combustion gases pass through the checker-brick in the carburetter and superheater, heating them, and the products of combustion are finally discharged at the outlet of the superheater. By proper adjustment of the time and intensity of blasting, the proper heating of the bed of fuel and the proper heating of the checker-brick are simultaneously completed without the loss of any unburned gases from the superheater outlet. When the heating operation is properly completed the temperature of the checker-brick will range from 2000° or 2200° F. at the top of the carburetter to about 1350° F. at the outlet of the superheater. Blast is then shut off, the apparatus is, by proper valves, sealed from the atmosphere, and the second part of the cycle—the production of gas or "run"—is begun.

In the run steam is admitted to the bottom of the generator fuel bed, rises through the bed, and, as stated in remarks under Table I, is decomposed by the incandescent fuel, forming a mixture consisting almost entirely of hydrogen and carbon monoxide, called uncarburetted or "blue," water gas (see Analysis No. 12). This gas passes to the top of the carburetter, and there receives a stream of injected oil. The oil is vaporized by the hot checker-brick, its vapor mingles with the water gas, and the mixture passes through the succeeding checker-brick in the superheater. In this passage the oil vapors are, as explained in remarks under Table I on destructive distillation, chemically changed and converted into other hydrocarbons, chiefly those which are permanent gases. (Note that the foregoing temperature of 2200° at the top of the carburetter would be sufficient to largely decompose and destroy the oil were it not that the absorption of heat in the vaporization of the liquid oil prevents this.) The gas then passes from this generating apparatus into the subsequent apparatus for the removal of tars, purification, etc. This production of gas is, of course, a heat-absorbing process, this heat supply being required for the decomposition of the steam (see remarks on hydrogen under Table I), the vaporization and destructive distillation of the oil, and the heating of these gases to the temperature of discharge at the superheater outlet.

In making the "run" it is found advantageous to alternate the direction of flow of steam and gas through the fire, the steam being admitted for a portion of the time at the top of the fire, and during the remainder of the time at the bottom. This system gives much better control of the temperature of the fuel bed: the flow of hot gas down through the bottom of the fuel bed preheats the fuel, making it more readily ignited by the succeeding blast, which results in an economy of fuel. The construction of the apparatus shown is such as to permit of this, there being an exit for gas from both the bottom and the top of the generator.

Analysis No. 13 is typical of the finished carburetted water gas. The composition of the gas (percentage of hydrocarbons, etc.) and its calorific power and illuminating power can, of course, be varied by varying the quantity of oil used.

The kind of fuel required for this water gas manufacture is one—anthracite coal or coke—containing very little volatile matter. If much volatile matter be present, as in bituminous coal, the heat absorption required for the distillation of this volatile matter will tend to keep the temperature of the fuel below

the point at which combustion can take place and steam can be successfully decomposed; also, the efflux of gas formed from the volatile matter must tend to prevent the contact of steam with the fuel, thus further preventing the decomposition of the steam. Though bituminous coal has, to slight extent, been used in water gas generators, its conversion into coke, after being charged upon the fuel bed, must be completed before it will successfully effect the decomposition of steam; this slow process has prevented its successful use for water gas manufacture.

## Producer Gas.

The use of this gas is so common and the theory of its production so simple that little explanation of the subject is necessary. There are, however, a few points worthy of brief attention.

As is stated in remarks under Table I, if air be supplied for the combustion of a bed of solid fuel, the products of combustion will generally contain both CO<sub>2</sub> and CO, the former decreasing and the latter increasing, in percentage with increase in temperature of the fuel bed. Starting with a moderately hot fuel bed and maintaining, for instance, a constant air supply, the temperature of the fuel will continually rise. As it does so, the percentage of CO formed increases, and, from the heats of formation of CO2 and CO (see Table I), it is evident that the heat generated by the constant air supply will decrease until finally a state of equilibrium is reached, the sensible heat of the producer gas issuing from the fuel bed equalling (neglecting the incidental losses by heat radiation, etc.) the heat generated by the combustion in the fuel bed; this prevents any further rise of the fuel bed temperature. In the remarks on carbon monoxide under Table I it was stated that in the combustion of pure dry carbon with dry air, both supplied at 60° F., and with exceedingly slow flow of air and gas, giving time for complete chemical equilibrium, the temperature of gas and fuel bed will be about 2250° F., and practically no CO2 will be formed, but only CO. In practical work the conditions and results will not be such; they are modified as follows. The rate of flow of air and gas must be quite rapid, and, with the large interstices and irregularities existing in the fuel bed, the gas and air will not come into such contact with the fuel that chemical equilibrium can become complete for the temperature, which will mean the formation of less CO and more CO<sub>2</sub>, and this will, in turn, mean higher temperature of both fuel bed and gas; also, there will be a slight heatrecuperating action of the fresh fuel as it heats and descends into the producer, this tending to increase the temperature in the hottest belt of the fuel bed. On the other hand, the fuel practically used will contain some mechanically-held moisture and some volatile matter, and the evaporation and distillation of these and the heating of their vapors will absorb heat; also, there is unavoidable loss of heat by radiation, etc.; also, ash exists and must be heated; these actions tend to lower the temperature of fuel and gas. With dry and good fuel the net effect of all the foregoing actions would be to produce a temperature in the hottest part of the fuel bed higher than the foregoing 2250° F. It is undesirable, however, that the fuel bed and gas shall attain so high a temperature for the following reasons; it will generally melt ash so as to form troublesome clinker in the fuel bed; also, if the use of the gas is such that it must be cooled and purified before burning, its high temperature means much more heat wasted, or recovered with added expense. Instead, therefore, of permitting so high a temperature of fuel bed and the carrying away of so much sensible heat in the issuing gas, a portion of this heat is utilized for the production of additional combustible gas; the method generally adopted is one of the following two:

I. Steam is admitted, mixed with the air supply, to the fuel bed and is decomposed, producing "blue" water gas mixed with the producer gas proper. The reactions, and the cooling effect upon the fuel bed and gas, are indicated in remarks on hydrogen under Table I.

2. Products of complete combustion of carbon (nitrogen and CO<sub>2</sub>) are returned, mixed with the air supply, to the fuel bed. A portion of the CO<sub>2</sub> is decomposed by the hot fuel, forming CO, each one volume of CO<sub>2</sub> decomposed yielding two volumes of CO, which means that for each one pound of carbon contained in CO<sub>2</sub> which is actually decomposed by the fire two pounds of carbon (or an additional pound) will be carried away from the fuel bed. From Table I it will be seen that the decomposition of the CO<sub>2</sub> containing one pound of carbon will absorb 14.544 B.T.U.'s, while the formation of the resulting CO containing two pounds of carbon will evolve only 8700 B.T.U.'s; there is, therefore, a strong cooling action on the fire, which will be

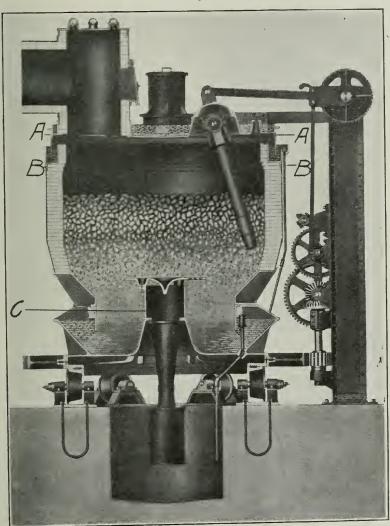
increased if, as is generally the case, the products of combustion returned to the fire are of a somewhat low temperature. method has the superiority to the foregoing steam admission method that the products of combustion used can be those formed from the producer gas itself when burned in engines. furnaces, etc., and can thus be circulated indefinitely, whereas in the foregoing process of simple admission of steam to the fuel bed this steam must finally be discharged to the atmosphere (in waste products of combustion), and its sensible heat and latent heat of evaporation thus wasted. This process yields a producer gas which is considerably diluted, and which will have, when burned, from either a hot or cold condition, a lower flame temperature. This last fact is in some cases an advantage; for instance, in furnaces it yields a more uniform, even though lower, temperature, and thus avoids possible danger to brickwork, etc.

Because of its heavy dilution with incombustible nitrogen, cold producer gas, when burned, gives a lower flame temperature than coal gas or carburetted or uncarburetted water gas (see remarks on flame temperature); also, its flame is more easily extinguishable, or is more "tender"; also, because of its low calorific power and its heavy weight, it is more expensive to distribute. These facts cause its use to be generally confined to the locality of its generation, and it is, moreover, preferable, where its use will permit, both for heat economy and to permit of its giving a high flame temperature, that it be burned in its heated condition as it issues from the generating fuel bed; for such use as for gas engines, which is exceedingly extensive, it must, however, be used cold.

The fuels used for the manufacture of producer gas can be any of the solid fuels shown in Table II; large quantities of even lignite and peat are used in certain localities, though it is generally preferable to use a good grade of bituminous or anthracite coal. The foregoing fully explains the formation of gas where anthracite coal or coke is used. Where bituminous material is used the volatile combustible is driven off by the heat of the fire, and then the production of the producer gas proper from the resulting coke takes place. If the distilled hydrocarbons, etc., from the volatile combustible be removed (mixed with the producer gas proper) from the producer without excessive heating and

consequent decomposition, it will give a gas of materially greater heating power, of higher flame temperature, and which is capable,

FIG. 9.



Hughes producer.

because of the presence of the hydrocarbons, of being burned with a somewhat luminous flame of greater heat radiating power,

which is desirable in some furnace uses; also, such treatment of the distilled and volatile matter renders possible the recovery of tar and ammonia, which are protected from destruction by excessive heating. This object, if desired, is attained by the removal of the distilled gases from the producer close to the point where the coal is charged. If, however, the foregoing is not desired, the design of the producer is such that the hydrocarbons, etc., distilled from the volatile matter of the coal are caused to pass through the highly heated portion of the fuel bed, and are thus broken up by excessive heat more nearly into their elements, carbon and hydrogen; this converts the heavy vapors, which would otherwise be deposited as tar, in great part into fixed gases, and this greater freedom from tar and vapors is an advantage in some cases.

The above illustration represents a producer, suitable for the use of bituminous fuel, and of the form alluded to in the above general remarks, in which the hot producer gas proper passes off through the top of the fire, assisting in the distillation or carbonization of the bituminous fuel, and carrying this distilled gas directly from the producer without its further decomposition by heat.

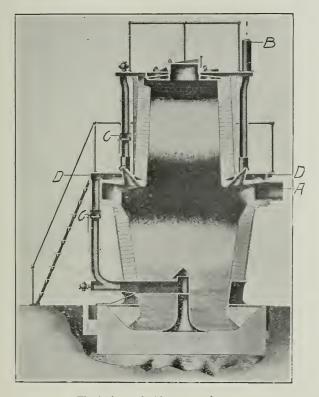
The cover (AA) of the producer is stationary. The body of the producer (BB), together with the fuel bed, is continuously rotated by the mechanism shown.

Bituminous fuel will generally, on being heated, melt or assume a plastic condition, which will interfere with the flow of the air and producer gas. In this producer provision is made for the continual breaking up of this plastic coal, and also the agitation of the general fuel bed and the working down of ash to the bottom. This is effected by means of the long arm shown, which projects down from the stationary cover into the fuel bed. This arm continually rocks back and forth, and as the body of the producer with the fuel bed is rotated there is thus produced a continual breaking up of the fuel.

The air and steam supply for the fuel bed are forced into its bottom through the vertical tuyere (C) shown. By means of the annular opening at the base of the producer, which contains a water seal for the prevention of communication with the atmosphere, the ash can be removed as desired.

Fig. to shows another form of producer suitable for the use of bituminous fuel. In this form, however, provision is made for the exposure of the gases distilled from the bituminous coal to a higher degree of heat, thus more thoroughly gasifying the heavy vapors and tars.

Fig. 10.



Westinghouse double zone producer.

The coal is charged upon the top of the fuel bed. The air supply for the combustion of the fuel is admitted in two parts, one over the top of the fuel bed and the other through the tuyere at its base. The air supplied to the top of the fuel bed produces a partial combustion sufficient to supply heat for the carbonization, or coking, of the coal, the coke thus formed then descending and its combustion being completed in the lower part of the producer. The producer gas with its contained vapors distilled

Vol. CLXXVI, No. 1051-4

from the coal, from the top of the fire passes downward through the hot fuel and is removed through the pipe (A) at the middle of the height of the producer; the producer gas formed at the bottom of the fire rises and is discharged through this same pipe.

This producer is of the "suction" type, the producer gas being drawn off by an exhauster, and this suction draws in the air supply for combustion through the inlet (B). By means of the valves (CC) shown the total air supply for the producer is divided between the top and the base in any desired proportion.

The air supply, before its admission to the fuel bed, is passed over water which is used for cooling the producer head, and also over the water contained in the annular ring (DD) at the middle of the height of the producer, which latter is heated by the waste heat of the offgoing producer gas; the incoming air is thus charged with the water vapor necessary for supply to the fuel bed.

The water-sealed opening at the bottom of the producer permits of the removal of ash as desired.

The breaking up of the plastic fuel, working down of the fuel bed, etc., is, in this producer, effected by hand stoking. Stoking holes are provided for this purpose in the head of the producer and also at various points in the ring DD, which afford ready access to all points of the fuel bed.

# Oil Gases.

The method most generally employed for the production of gas from oil is that of simple destructive distillation. process the oil is introduced into a closed vessel or retort and subjected to heat. A temperature of 700° or 800° F. will, in general, suffice for the practically complete vaporization of even heavy crude oils. As explained under Table I, however, these vapors would, if subjected to atmospheric pressure and temperature, immediately recondense to the liquid form. They are, therefore, subjected to a still higher heat to transform them into permanent gases. It is very generally desired to thus produce an oil gas which shall have both high heating power per cubic foot, and also high illuminating power. Analysis No. 11 represents such a pure oil gas, and this is also approximately the quality of oil gas which, mixed with uncarburetted, or "blue," water gas, is produced in the manufacture of illuminating carburetted water gas (see Analysis No. 13); the temperature which July, 1913.]

the oil vapors must attain for such gasification is about 1300 to 1400° F. Under higher temperature of gasification than the foregoing there is further decomposition of these oil vapors into their constituents, free carbon and free hydrogen. Analysis No. Io is that of an oil gas (intended for balloon inflation) formed by passing the oil vapors through a very hot bed of incandescent carbon (coke); it will be observed that there has taken place very great decomposition of the hydrocarbons into free carbon and hydrogen, the heavy vapors (illuminants) having been practically all destroyed, and the resulting gas being of very feeble luminosity. It is, in general, impossible to convert all of the oil into a mixture of permanent gases and vapors capable of transportation; a considerable portion of the vapors will be so heavy that they are incapable of carriage even when heavily diluted with permanent gases, and these vapors, mixed with free carbon, will be thrown down at the outlet from the generating apparatus in the form of tar.

A very considerable quantity of gas is also manufactured by mixing the oil vapors with steam in the foregoing destructive distillation process. At the temperature of gasification of these vapors, some of this steam will undergo decomposition by the portion of free carbon liberated from the oil gas, and there will thus be formed a mixture of oil gas and uncarburetted water gas.

With the kinds and uses of oil gas you are probably all pretty familiar. Large quantities of oil gas, of the quality represented by Analysis No. 11, are manufactured, compressed into portable reservoirs, and used for car, etc., lighting; this gas endures the high degree of compression employed in this use (15 atmospheres even) without serious loss of volume, heating power, or luminous power. Very considerable quantities of oil gas are manufactured, by the process indicated in the preceding paragraph, from the very heavy crude oils of the West, and used for public gas supply. Another interesting modern form of oil gas supply is to compress a gas of the general quality shown by Analysis No. 11 under a pressure of about 100 atmospheres. thereby liquefy roughly one-half of it, and deliver this liquid product in strong steel capsules for domestic use; on releasing this liquid, in whatever quantity is desired, from the capsule it is so volatile that it at once reassumes the gaseous form ready for use; there is thus obtained from the portable liquid gas of high heating power at any burner pressure desired.

Hallwachs-effect in Selenium. G. Zoltán. (Phys. Zeitschr., xiii, 454.)—Selenium was melted on a metallic disk and cooled rapidly. Some preparations were annealed at 217° C. to convert the selenium into the gray crystalline modification. The metallic plate was made the negative plate of an air condenser and was illuminated by a mercury lamp and charged by a water battery. The other plate of the air condenser was connected with a quadrant electrometer. The Hallwachs photoelectric current was measured by the angular speed of the electrometer needle, recorded on a chronograph. The results show, (1) in the case of crystalline selenium, that the photoelectric sensitiveness increases after the time of preparation, especially if kept in the light; the sensitiveness is increased by positive electrification at ordinary or low pressures, but reduced by negative electrification in the open air. (2) In the case of amorphous selenium, the sensitiveness is reduced by light and recovers in the dark. Negative electrification diminishes sensitiveness, while positive electrification increases it.

Efficiency of Illuminants. C. P. Steinmetz. (Electrician, lxx, 346.)—It is pointed out that besides the efficiency of the illuminant such questions as the distribution of light, intrinsic brilliancy, and color are important. But practically any distribution curve can be obtained by suitable shades and reflectors, etc., although with some loss of light. A bad natural distribution curve is therefore a disadvantage, and so is a high intrinsic brilliancy. In correcting either of these defects a loss of from 10 to 30 per cent. may be incurred. Color has a direct influence on efficiency; bluish-green light is probably the most efficient radiation at low illuminations. A diagram is given showing the efficiency in candle-power per watt, plotted against the energy and consumption of various illuminants. The highest figure recorded for the titanium are and yellow flame-are is about 5 candle-power per watt.

High Tropical Winds. W. VAN BEMMELEN. (Nature, xc. 250.)—Observations of pilot balloons in Batavia confirm the existence of a high westerly wind above the trades and anti-trades, and immediately below the persistent easterly winds which are peculiar to the tropics, and which carried the dust from the Krakatoa eruption of 1883 many times round the earth at a level of about 30 kilometres. The order of the currents is as follows: (1) Shallow local breeze; (2) southeasterly trade wind to 3 kilometres; (3) northeasterly anti-trade to 17 kilometres; (4) upper southeasterly trade wind to 18 kilometres; (5) high westerly wind to 23 kilometres; (6) easterly Krakatoa wind to at least 30 kilometres. The velocities of the currents numbered (2), (3), (5), and (6) are about 5, 16, 12, and 35 metre-seconds respectively.

#### THE ELECTRICAL PROPULSION OF SHIPS.\*

BY

#### W. L. R. EMMET, Sc.D.,

Consulting Engineer and Engineer of Lighting Department, General Electric Company.

MR. EGLIN has done me too much honor in introducing me as one of the foremost authorities on steam turbines in the world, because my function has been largely that of a developer of apparatus and enterprises, rather than that of an inventor, although incidentally I have done a certain amount of inventing.

Parsons is the great pioneer of the turbine, and De Laval is another who is entitled to great honor, and next to them comes Curtis, who after these other men had worked for a long time, for possibly eighteen years on the development of the turbine, it had only reached a small stage of advancement; that is, commercially. Mr. Curtis conceived an idea which was quite different in some respects from those previously designed, and which made the turbine somewhat more flexible as to speed, and introduced in it a number of practical characteristics which helped its advancement.

My part in connection with the turbine has been that of developing the Curtis turbine. Within two years after I undertook to work on the turbine, we had four or five times as many in operation as we had ever seen, and something like four times as large turbines, and that may have done something to stimulate the growth of the turbine and the advancement of it. That was the beginning of the turbine, but, so far as our interest is concerned, it began about 1901, and by 1903 we had turbines as large as 700 kilowatt capacity, stations as large as 7000 kilowatt capacity operating, and therefore the industry reached at a bound a high state of development, and then the reciprocating engine for making electricity went out of favor; this was probably within two years after we began building turbines and

<sup>\*</sup> Presented at the joint meeting of the Electrical Section and the Philadelphia Section, American Institute of Electrical Engineers, held Thursday, January 9, 1913.

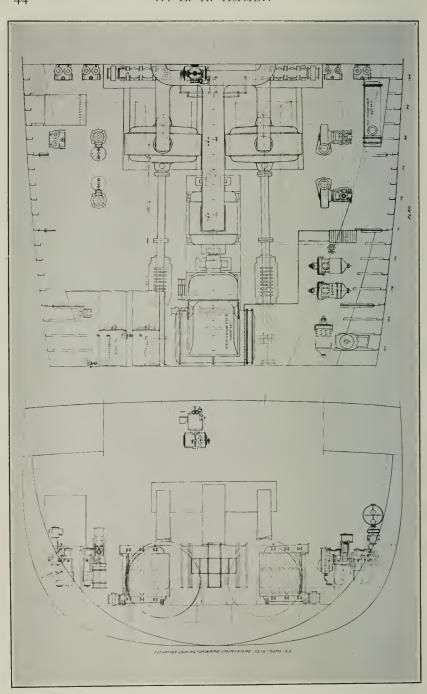
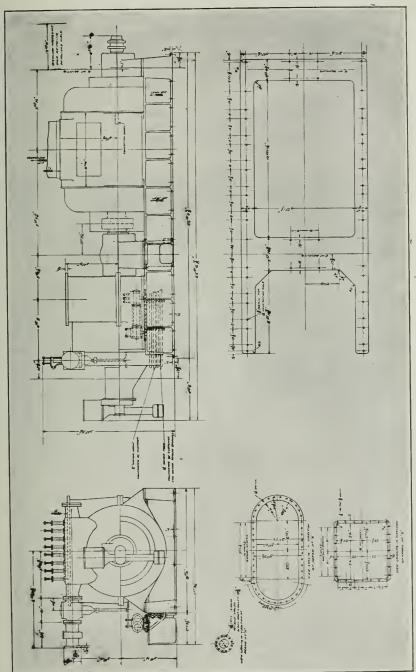


FIG. 2.



Outline of generating unit, U. S. collier Jupiter.

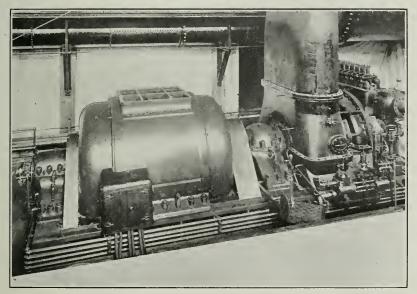
advocating turbine stations. I suppose in the earliest stage of the turbine for driving electrical machinery the idea was suggested of driving a ship by the turbine and motor. The idea has previously been discussed in connection with storage batteries. When Plante first demonstrated the principle it was said that ships would be driven across the ocean by storage batteries; there was some boat work done with storage batteries. You will remember that boats were propelled in that manner at the World's Fair, but the storage battery is too heavy and too inefficient, and its period of economical storage is too short to make anything like ship propulsion possible by its use, and all the methods of production of electricity known heretofore were such that they offered no inducement for driving ships by electricity.

Now, in what I am going to show you to-night and explain to you, there is very little of invention; it is simply an engineering evolution and development, at a certain stage of development which justifies certain proceedings and justifies the prediction of certain results. And the question remains as to whether those results are good enough to compete with other methods that apply to the propulsion of ships. The industry of propelling ships is one of the greatest engineering industries of the world. Many people do not realize the immense amount of power used in driving ships. It is safe to say that the power in the *Lusitania* would drive the electric railways of Philadelphia. I am not quite certain in that statement, but it is very nearly so; it would certainly do so for many hours of the day. That is only one ship of thousands.

The horsepower capacity of Parsons turbines which had gone into ships from 1905 to last year was reported at something like 9,000,000 horsepower, which is in the neighborhood of three times as much as the total output of turbines by the General Electric Company in ten years, and more than twice the total output of turbines in the United States; such a capacity has actually been put in ships in six or seven years to drive them with Parsons turbines. The only ships to which turbines have been applied are the very fastest vessels; turbines are suited to use in nothing but the fastest ships, and even there are relatively unsuitable. As time has gone on we see the turbine has been improved and put into positions of prominence. As a pro-

peller of ships where it may be driven at high speeds, at the time of its sudden rise to prominence it was a very noticeable piece of machinery, and its economies were simply an approximation of those which were supposed at that time were possible. When I advocated this tremendous plunge in turbines and took the responsibility of jeopardizing millions of dollars of my employer's money in going into this enterprise. I had no idea that the turbine was as much better than the engine as it has proved,





Generating unit, U. S. collier Jupiter.

but was confident that, being better than the engine in the beginning, the reason for its use would increase.

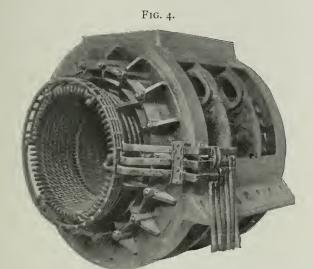
When we first began to build turbines, the speeds of them were relatively low, but they were high compared with reciprocating engines, but were low as compared with those which we can now build. The generators which were used to make electricity from the turbines were at that time very radical in the matter of speed, and they were a matter of terror to people who were going to use them. The centrifugal strains were great; but as time has gone on we have developed better methods, and,

while we at first feared to build a high-speed generator, we have for some time past had such success in building high-speed generators that the limit has been in the turbine. There have been certain limitations in the speed of the turbine which determined the capacity of a unit of a given speed. But very recently, since the publication of any of my papers on electrical propulsion of ships, this speed limit has been raised by the development of a means of designing a turbine which has enabled us to get the highest efficiency with very high speed, and this change has brought with it an added reason for advocating ship propulsion by electricity.

Now the net result of all this is that when we began to build turbines we could just beat the reciprocating engine that was then used for making electricity. Our machine was better and a little more efficient, but very slightly. Its increased efficiency was due almost entirely to the fact that a turbine is a machine in which you can use the full expansion of steam, whereas a reciprocating engine is a machine in which you cannot use the expansion of steam. The volume of steam with the vacuum which is customary in power stations is something like 200 times as great as the volume of steam which issues from a steam boiler. The curve of the expansion of steam is, as you know, a hyperbolic curve, and the areas of these long ranges of expansion are enormous. A reciprocating engine working condensing, with the best vacuum obtainable, is only about 25 per cent. better than a reciprocating engine working non-condensing, and the turbine is 100 per cent, better condensing than the turbine working noncondensing.

As time has gone on the turbine has become more and more efficient, and with the improvement in details, such as relative velocities, bucket shapes, the direction of the steam against the blades, etc., a very high efficiency has been reached, and we now have a turbine taking out 75 per cent. of the power—in fact, 76 and 77 per cent.—whereas, with a reciprocating engine through the best part of its range is not getting more than 76 and 77, and the reciprocating engine is working on a very much narrower range. The turbine's efficient range is from 250 pounds per square inch right down to any vacuum that can be produced, to 29 inches, and the means of producing vacuum have been improved in connection with turbine work.

The net result of all this is that the best reciprocating engines making electricity are producing, at their best point of power, about 18 pounds of steam per kilowatt, whereas with turbines



Stator frame and windings of generator, U. S. collier Jupiter.

we are down as low as 11 or 11.5. I think possibly that that statement is somewhat unfair, because superheated steam enters into that, and I will say that perhaps about 18; 13 would be a





Revolving field of generator, U. S. collier Jupiter.

fair ratio of comparison of the best turbines of to-day with the reciprocating engine existing before turbines were begun. On board ship the reciprocating engine is subject to just as great limitations as it is on shore, and in some cases it is subject to

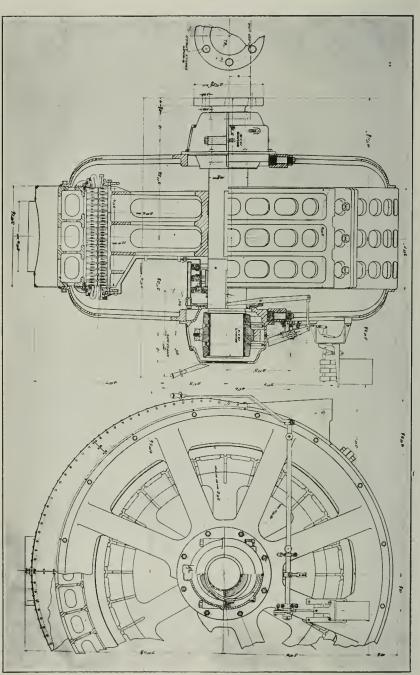


Fig. 6.

very much greater limitations. The difficulty about making reciprocating engines for economy is that the low-pressure cylinders become very large and heavy, and the valves and steam connections have to be made very large in order to get good economy. On board ship this is a very severe limitation in output. For instance, in a battleship, which has to make occasional high



Stator of motor for U.S. collier Jupiter.

speed, the engines, if of reasonable weight, must be badly congested when she runs at this maximum speed. In the first turbines made some of the same limitations existed to a certain extent; but the improved methods of building turbines have gradually eliminated these difficulties and made the turbine work effectively through a wider range, and made it smaller for its output on account of increased speed. This development had gone on for some time before it reached a point where electrical propulsion could be considered justifiable. In the *Mauretania*,

which is the best example of a turbine-driven ship, the turbine propeller speed is about 180 revolutions per minute, and each of the turbines has a capacity of about 17,500 horsepower. For shore purposes we make a turbine of 17,500 horsepower which runs at 1500 revolutions per minute. We could make it as high as 1800 revolutions per minute, so that the speed of our turbine for shore purposes is 10 times as high as those designed for shipping. This great difference of speed enables us to make the turbine extremely light. The desirable speeds of a ship's turbine and an electrical turbine may have a ratio of 10 to 1, and the size of the turbines is nearly in the same ratio. On the other hand, the propellers of the turbine ships are run at the limit of the speed in order to help the turbine, and these propellers are put far above the speeds which would be selected if the turbine itself was not considered. Advocates of ship turbines have done a great deal of work on high-speed propellers, and their arguments have all tended to crowd up the speed limits. The best authorities show wide variations of efficiency through such ranges of speed as are covered by these differences. The propulsive efficiency of ships is very low. It ranges from 45 to 60 per cent., possibly, and it works through ranges which are very large as compared with the variations of efficiency which we ordinarily consider in prime movers. tricity affords a means by which we can adopt any propeller speed we please, and we can also adopt any turbine speed, and the desirable turbine speed and the desirable propeller speed being as they are, in many ships we find the ratio we would select is 18 or 20 to 1. That is, we run the turbine 18 or 20 times as fast as we run the propeller, whereas in the turbine ships these two are forced together.

Now when this possibility of driving a ship by electricity began to loom up as an attractive proposition the question of gearing was discussed and advocated; that is, gearing helical spur type. The difficulty in the application of gearing to a ship varies with the rate of reduction necessary. It is easier in gearing anything to effect a small ratio than a high ratio, and the effective gearings that have been made up involve a rather small ratio of gearing.

The Parsons turbine is susceptible of a very good design for

moderate speeds. It is not very good for the extreme limits of capacity in high speeds, but for certain intermediate speeds it gives very good efficiency without very much complication, and it is therefore made quite attractive if we can have a gear with even a moderate reduction between the propeller and the turbine.

Sir Charles Parsons, who is a great engineer and a great man, has always done good work in everything he has ever



Rotor of motor for U. S. collier Jutiter.

touched. He has worked on this gearing a good deal and has got some very successful results, and the prospect of using gearing and the discussion of the possible use of gearing have tended to retard the development of electricity as a means of speed reduction.

Mr. George Westinghouse also has done some very excellent and interesting work on the development of gears for driving ships, and the gearing on the *Neptune* is a very good example. The turbines in her are not efficient, and as an engineering prop-

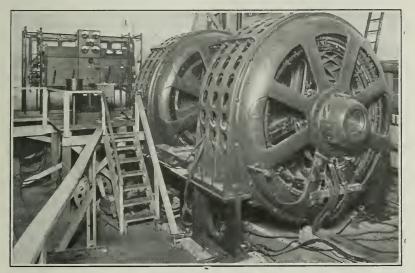
osition she was badly handled, so that the ship never had as good results as she ought to; but the gearing has been successful, so that we must regard gearing as a factor, and we must not say that electricity is justified because the gearing is not practicable. All indications are that the gearing is workable and is good. Large vessels will be harder to drive effectively by gearing than small vessels. The scope of the application of gears is unknown. They have only been applied to a limited extent, and we can see all kinds of difficulties as we go forward, but it is safe to say the gear will have an application; at least in smaller vessels it will be cheaper than electricity, and should have an extensive use.

However, the recent developments of the turbine have improved the prospects of electric propulsion so much that it would appear that no possible development of gearing could bring it to an equality with electricity as a means of speed reduction for large ships. In certain classes of vessels, as I say, we now can make turbines as high as, sav, 25,000 horsepower with a speed of 1800 revolutions per minute, and these turbines have an efficiency of 75 per cent., and they are so small and so compact that it is enormously advantageous in a ship to use them. The electrical apparatus involves a certain weight, and weight involves a certain loss, but in large vessels that weight and loss is small and relatively unimportant, and the simplicity of electrical reduction is entirely in its favor, although people unfamiliar with the use of electricity have been disposed to think badly of it on the score of complication. The electrical machinery for this purpose is so well known that any engineer can analyze the designs proposed, and he cannot condemn them on the ground of possible trouble, for the reason that all sorts of machinery are being run by electricity under greater difficulties. In the case of ship propulsion the matter is particularly simple, because we only make as much electricity as we require, and we simply supply what we need, and there is no trouble from short-circuiting, and the largest power that comes from the generator is incapable of burning out any conductor in it. There is no waving conductor in the system, and the voltage is low. It is convenient for installation, and the voltage and the character of the apparatus is such that in twenty years of experience

on shore with that particular kind of apparatus and voltage there is hardly a single case of insulation failure.

The method which we propose for propelling ships by electricity is the combination of a simple 3-phase alternator with induction motors. Such design is used in the *Jupiter*, now being built on the Pacific coast. Her motors have resistances in their secondaries, which resistance is needed in getting a large torque to reverse. We have recently devised ingenious





U. S. collier Jupiter-Motors set up for test. One being used as a generator to load the other.

means in motor design by which we can dispense with that resistance and can reverse the propellers without this complication. The rotor becomes a squirrel-cage design, and the only high-voltage, current-carrying conductors in the system are on the stationary parts. This is a great advantage, and we have also developed it in such manner that we can stop, start, and reverse by simply opening and closing switches without disturbing the excitation. There has been, in connection with this development, so much designing that it is a little difficult to say where to stop in explanation. You want to remember that the object is speed reduction and the method is fundamentally

Vol. CLXXVI, No. 1051-5

Fig. 10.



Water-cooled rheostat, U. S. collier Jupiter.

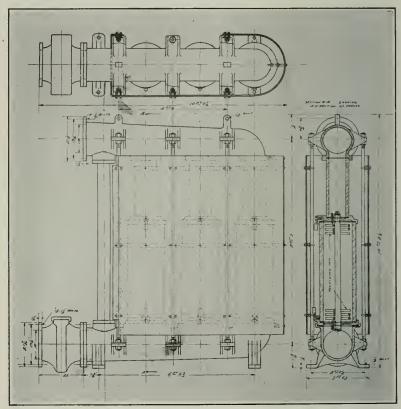
simple as compared with the simplest apparatus that is used on shore for general purposes.

Among the pictures which I will show you are curves relating to the collier Jupiter, now being built at the Mare Island Navy Yard, a ship of about 20,000 tons capacity displacement. She is a sister ship to the Neptune, which has been fitted with the Westinghouse gears, and of the Cyclops. The Jupiter will be equipped with turbines and will be run, I think, about next May. We first built the Jupiter's apparatus under certain specifications which we made for the Government. We made certain predictions as to results which would be accomplished, and we made certain guarantees. The test of the apparatus last June showed the performance was slightly better than our prediction—190 pounds steam pressure and 28.5 inches vacuum and saturated steam would give 12 pounds per horsepower on the propeller shafts; but just previous to these tests we began to get new light on the matter of turbine design; we found means to produce better efficiency. I was very anxious at that time to get the earliest possible data on these improved methods, because it was useful to us in much of our work, and, while the Jupiter had met our predictions, I also wanted to get the best standard of efficiency in this installation. The new type of design being simpler than that first built, we decided to change the generating unit, and we got permission from the Government to make the change.

We recently tested this new generating unit, and the results produced by it bring the water rate .9 pound lower. It will be about 11.1 pounds per shaft horsepower under the conditions I have stated. This generating unit has given results far better than anything that has been produced from any turbine unit in the world. About the best recorded performance of a turbine which had previously been generally credited was that of a Parsons turbine in Dunston Station, in Newcastle, England, accounts of which were published about a year ago. This machine, with 220° superheat and 29 inches vacuum, produced an efficiency of 68.6 per cent. In our test we could not produce such a high degree of superheat; we only tested at a little above 100, but we tested it at various degrees of vacuum. The projection of our curves to the same degrees of superheat and

vacuum as at Dunston Station shows an efficiency of 73 per cent., as against 68.6 per cent., which is a pretty big gain to make in a prime mover; so that, while the *Jupiter* was only a moderately good case for electric ship propulsion by electricity, we will

Fig. 11.

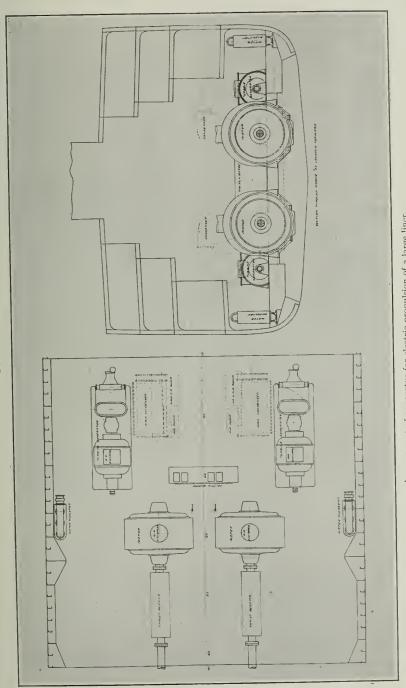


Water-cooled rheostat, U. S. collier Jupiter.

make a pretty good demonstration. I think that since this contract has been made the interest in this subject has steadily increased and grown.

We have been figuring recently—through the British Thomson-Houston Company—on a very large ship in England. and the results we show, based on actual tests of apparatus at Schenectady as possible on that ship, are so good that the owners





Arrangement of apparatus for electric propulsion of a large liner.

simply cannot turn their back on it, especially if the demonstrations on the *Jupiter* show that the methods are entirely practicable, as we are sure they will.

I learned to-day that we will probably get an order to equip a large and fast yacht. This vessel will have a relatively small power, and in this respect is not very well suited to electric propulsion, but on account of the high-speed turbines and improved designs which we have developed the case works out very well and is in every way attractive to these people. This case is something like that of a warship, because they want to run at an economical cruising speed as well as an economical high speed. In my designs as applied to merchant ships the turbine is slowed down for low speed, but in the case of warships we arrange to change the ratio of speed reduction by connecting for different numbers of poles so that we can run with one range for high speeds and another range of reduction for low speeds, and we will probably do the same with this yacht with a certain degree of advantage, though not as much as we get in the warship; if this is done, it will demonstrate the practicability of the method for warships.

The Jupiter is designed for a speed of 14 knots; the Cyclops made 14.6 knots in her trials, and this vessel has equivalent boiler capacity. She is designed with a view to receiving reciprocating engines, and the turbines are simply put in the space which the reciprocating engines would occupy, and our contract reads in such a way that if we do not do all that we predict our machinery will be lifted out on the dock and the reciprocating engines put in, and there will simply be a little time lost. I think it proper that the Government should have made due provision for the possibility of substituting reciprocating engines, because this method is new. I am very sure that when this ship has been run the general fear of electrical propulsion will change, because she will be successful. I say this because I am an electrician and am familiar with electricity. It is the easiest thing I do. Other people have a different view of such things and have not acquired the electrical habit. When they do acquire it, they will want to do everything by electricity, and they will in most cases be right.

### NOTES ON ELECTRIC FIELD DISTRIBUTION.\*

#### BY

### W. S. FRANKLIN,

Professor of Physics, Lehigh University.

Member of the Institute.

Several of my former students have asked me where they might look up the electrostatic theory that is necessary to fully understand the important paper which was read before the American Institute of Electrical Engineers, on March 14, by Mr. C. Fortescue, on "Insulation Problems," and, in view of these requests, it seems worth while to publish the following discussion of Mr. Fortescue's paper which was given before the instructing staff and students of the Departments of Physics and of Electrical Engineering at Lehigh University. The discussion is made as brief as possible, and it is assumed that the diagrams will make the meaning clear.

The following propositions are extensively used in theoretical discussions of electrostatics:

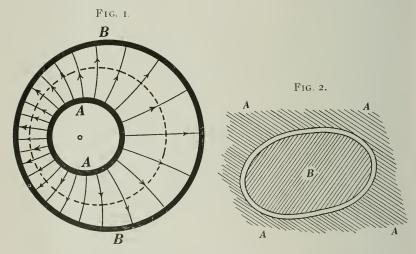
- (a) Any equipotential surface may be wholly or in part replaced by a thin metal sheet without disturbing an electric field distribution. Thus Fig. 1 shows the lines of force between two metal cylinders A and B. The dotted line represents an equipotential surface, and this equipotential surface may be replaced wholly or in part by a thin metal sheet without disturbing the field between A and B.
- (b) A closed metal shell screens its interior from all outside electrostatic effects. This action of a metal shell may be understood in terms of a mechanical analogue as follows: Fig. 2 represents a mass of steel B completely separated from a surrounding mass of steel A by an empty space. The steel B remains unstressed however the steel A may be stressed, because stress cannot be transmitted across an empty space. Fig. 3 represents a mass of dielectric B completely separated from the surrounding dielectric A by a metal shell. The dielectric B remains unstressed however the dielectric A may be stressed,

<sup>\*</sup> Communicated by the Author.

because electrical stress cannot be transmitted through metal. A very rapidly changing electrical stress can, however, be transmitted through metal to a slight extent.

#### THE METHOD OF ELECTRICAL IMAGES.

It is easy to formulate mathematically the distribution of electric field due to an electric charge which is thought of as being concentrated at a *point* or along a *line*, and the formulation of ideal problems of this kind furnishes the basis for the solution of some of the important practical problems in electric field distribution. Thus the fine lines in Fig. 4 represent the



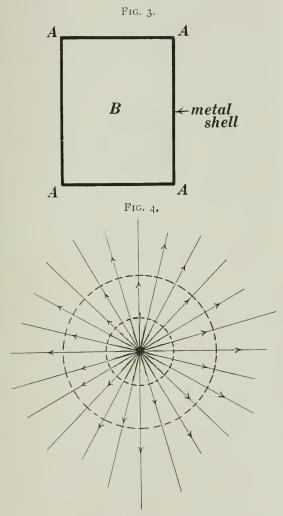
electric lines of force around a long, straight linear charge (a charge on a fine wire, the wire being very small and perpendicular to the plane of the paper). The potential at any point p in Fig. 4 is equal to

$$2Q \log_e r - 2 Q \log_e r_o$$

where r is the distance of the point p from the axis of the wire, Q is the charge per unit length of the wire, and  $r_0$  is the distance from the axis of the wire to the chosen region of zero potential. This expression for the potential due to a linear charge is fully discussed in most text-books on electrostatics.

The equipotential surfaces in Fig. 4 are cylinders, as represented by the dotted circles. If the inner circle, in Fig. 4, be

replaced by a solid metal rod and the outer circle by a hollow metal cylinder, as shown in Fig. 5, the electric field in the intervening space will remain unaltered. Therefore the distribution

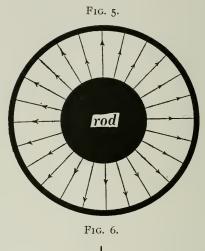


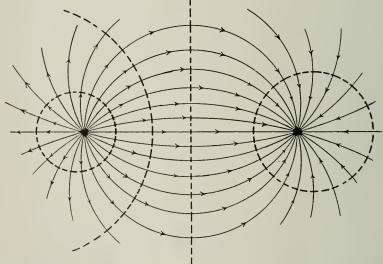
of electric field around an ideal linear charge as shown in Fig. 4 leads to the solution of the problem of the distribution of electric field in the insulation of a cable as shown in Fig. 5.

Fig. 6 shows the electric field distribution between two long, straight, parallel equal but oppositely charged lines, the lines be-

ing at right angles to the plane of the paper. The expression for the potential at any point p in Fig. 6 is

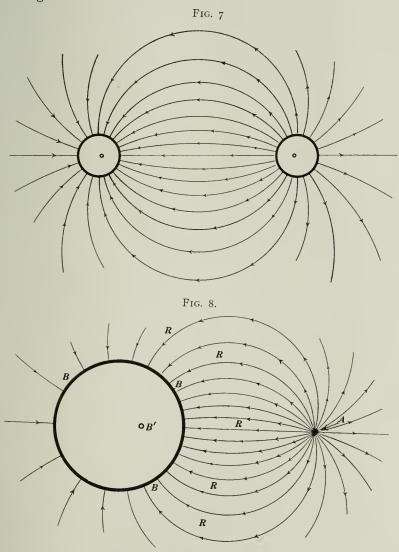






where Q is the charge on the lines per unit length, positive on one line, negative on the other,  $r_1$  is the distance of p from one line, and  $r_2$  is the distance of p from the other line. This ex-

pression for the potential due to two linear charges is easily found from the expression for the potential due to one linear charge.



The equipotential surfaces in Fig. 6 are circular cylinders as represented by the dotted circles, and the equipotential surface midway between the linear charges is a plane. Fig. 7 shows

two of the equipotential surfaces of Fig. 6 replaced by metal cylinders. The distribution of electric field between parallel metal cylinders as shown in Fig. 1 or Fig. 7 is the same as the distribution of electric field in Fig. 6. Therefore the mathematical formulation of Fig. 6 leads to the complete solution of the problem of electric field distribution around or between parallel cylinders. Approximate formulas are nearly always used in connection with the problem of parallel cylinders, however, because the rigorous formulas are rather complicated, as will be understood by reading pages 273 to 277 of Franklin's "Electric Wayes."

A great variety of particular problems relating to electric field distributions can be set up and solved by the method of images as exemplified by Figs. 1, 4, 5, 6, and 7; and the origin of the term electric image may be understood with the help of Fig. 8. The electric field distribution between a linear charge A and an oppositely charged metal cylinder BB is identical to the electric field distribution which would be produced in the region RR by a line charge at A and an opposite line charge at B'. The easiest basis for the mathematical formulation of the field RR in Fig. 8 is, therefore, to think of the field as being due to the two linear charges A and B'. The fictitious linear charge B' is called the electric image of A with respect to the cylinder BB.

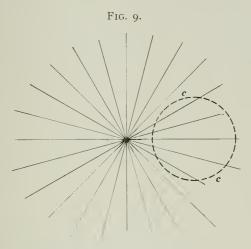
THE PRODUCTION OF ANY DESIRED FIELD DISTRIBUTION IN A REGION BY THE CREATION OF PROPER POTENTIAL VALUES EVERYWHERE OVER THE BOUNDARY OF THE REGION.

The distribution of electric field in a region depends upon two things; namely, (a) the potential values over the boundary of the region and (b) the distribution of electric charge in the region. When there is no charge in the region the boundary values of potential determine the field distribution. Therefore, if it is desired to produce any assigned field distribution in a given region (a field distribution which is not associated with electric charge in the region, or, as it is usually expressed, an electric field which has no divergence  $^1$  in the region), it is suffi-

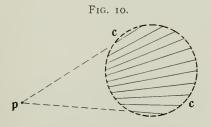
<sup>&</sup>lt;sup>1</sup>A very simple discussion of the important ideas of *divergence* and *curl* is given in Chapter IX of Franklin, MacNutt and Charles's "Calculus," published by the authors, South Bethlehem, Pa., 1913.

cient to create the proper potential values over the boundary of the region.

Example 1.—Fig. 9 represents the lines of force surrounding a linear charge. The dotted circle in Fig. 9 represents a cylinder parallel to the linear charge. Imagine this cylinder to



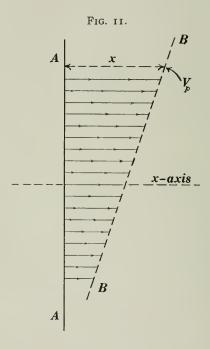
be made of narrow insulated strips of metal as represented by the separate dots of the circumference, and imagine each strip to be brought by proper means to a potential equal to the potential at the strip due to the linear charge in Fig. 9. We would thus have the potential fixed at every point on the dotted cylinder



in Fig. 9, and the electric field distribution inside of the cylinder would be as shown in Fig. 10, irrespective of the electric field outside of the cylinder. Fig. 10, therefore, is an example of the production of a desired electric field distribution in a given region by bringing the various parts of the boundary of the region to the proper potential values.

Example 2.—A metal sheet AA (Fig. 11) is at zero potential, and a series of insulated metal strips BB very close together and perpendicular to the plane of the paper are brought by proper means to potential values such that the potential  $V_p$  of any strip is proportional to its distance x from AA. Under these conditions the region between AA and BB will be a uniform electric field, as indicated by the lines of force in Fig. 11.

The method illustrated in Figs. 10 and 11 for producing any assigned electric field distribution in a given region is used by



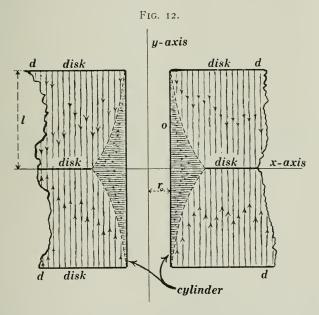
Mr. Fortescue in the designing of insulating structures. Let it be required, for example, to produce a uniform electric field parallel to the y-axis in the region of the coarse lines of force in Fig. 12, and a cylindrically radiating electric field in the region of the fine lines of force in Fig. 12. By cylindrically radiating field is here meant a field which radiates from the y-axis in an uncharged region.

Let us assume that the cylinder of radius  $r_0$  and the end disks dd are at zero potential, and let us consider the potential

at any point p of which the co-ordinates are x and y. The potential at p due to the radial field is

$$k \log_e x - k \log_e r_o$$

where k is a constant, on the assumption that the radial field reaches to p; and the potential at p due to the uniform field is fl—fy, where f is the intensity of the uniform field. The locus of the points where the two fields give the same potential is represented by the dotted curve in Fig. 12, and its equation is gotten by equating the above expressions for potential.

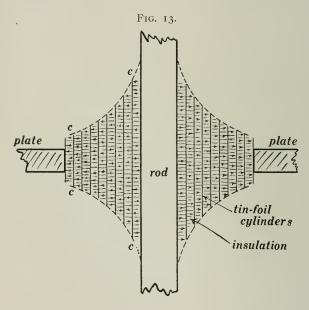


Now, in order that the two fields as indicated in Fig. 12 may be actually obtained, it is sufficient to have the tube and the end disks at potential zero, to have the middle disk at potential fl, and to provide a number of rings of tin foil (as represented in section by the dots of the dotted curve in Fig. 12) along the common boundary of the two fields, these rings being brought by proper means to potentials which conform to both fields.

The radial field of which the potential is

 $2Q \log_e r + a constant$ 

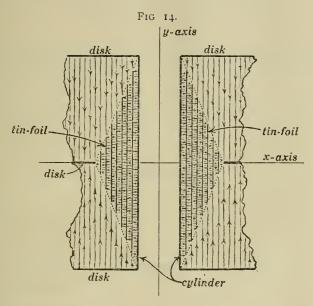
is the only type of field which can radiate from an axis in a region where there is no charge. If it is desired to produce a radial electric field which remains constant in value with increasing distance from the axis, it is necessary to provide a series of coaxial cylindrical leaves of metal as shown in Figs. 13 and 14. Fig. 13 shows the well-known condenser type of insulating bushing. The theoretically correct shape of the curve cc in Fig. 13 is an equilateral hyperbola, because in this type of bushing the successive tin-foil cylinders must have the same area. No attempt is made in Fig. 13 to represent the distribu-



tion of the electric field in the region surrounding the bushing. As a matter of fact, this electric field is very greatly concentrated in the region immediately surrounding the rod at the ends of the bushing.

Fig. 14 shows the method suggested by Mr. Fortescue for eliminating the concentration of electrical stresses at the ends of the bushing in Fig. 13. There is a constant potential difference between successive tin-foil cylinders in Fig. 14, and therefore, if the potentials of the successive tin-foil cylinders are to be conformable to the uniform electric field which is represented by the coarse lines of force in Fig. 14, it is necessary to ter-

minate the cylinders along the dotted straight lines as shown in Fig. 14. With this arrangement, however, the tin-foil cylinders do not all have the same area; and, therefore, to provide for equal potential steps between successive tin-foil cylinders, it is necessary to connect the successive cylinders to the proper points in the winding of the transformer.



UNIFORM ELECTRIC FIELD MODIFIED BY A CYLINDRICAL CONDUCTOR.

Fig. 15 shows the lines of force in the neighborhood of a metal cylinder of radius r in a region which would be a uniform field at right angles to the axis of the cylinder if it were not for the distorting influence exerted on the field by the metal cylinder. The mathematical formulation of the field distribution in Fig. 15 is accomplished by the method of images as follows:

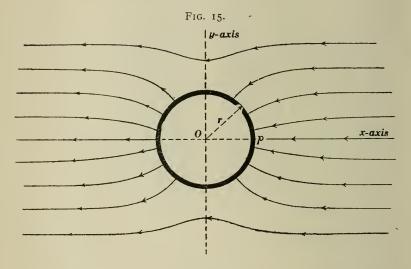
Consider two opposite linear charges parallel to each other and at a distance dx apart, and let +Q and -Q be the charges per unit length, where Q.dx is a finite quantity. Such a pair of linear charges is called a *linear doublet*, and the product Q.dx (=M) is called the *moment* of the doublet.

The potential at a point due to a linear doublet is found Vol. CLXXVI, No. 1051-6

with the help of Fig. 16 as follows: The potential at the point p in Fig. 16 due to the linear charge +Q is  $2Q \log_e (r + \triangle r)$ , and the potential at p due to the linear charge -Q is  $-2Q \log_e r_o$ . Therefore the net potential at p due to the doublet is

$$2Q \left[\log_e\left(r + \triangle r\right) - \log_e r\right] = 2Q \frac{d \left(\log_e r\right)}{dr} \cdot dr$$
$$= 2Q \frac{1}{r} \cdot dr = 2Q \frac{1}{r} \cos \theta \cdot dx = 2M \frac{\cos \theta}{r} \cdot dr$$

The finding of the mathematical formula for the distribution of potential in Fig. 15 depends upon the finding of an expres-



sion for potential which will give a constant potential over the surface of the cylinder, but which at great distances from the cylinder will reduce to the potential which is associated with the uniform field. This condition is met by superposing the potential due to a linear doublet upon the potential which is associated with the uniform field.

The above expression for the potential of a linear doublet is based upon the choice of the y-axis in Fig. 15 as the region of zero potential, and the expression for the potential which is associated with the uniform field in Fig. 15 is -fx, where f is

<sup>&</sup>lt;sup>2</sup> The undetermined constant 2Q loge ro is here ignored because it drops out anyway.

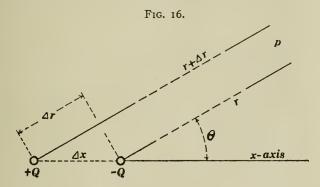
the intensity of the field. This field is directed toward the left in Fig. 15. Therefore the potential due to the uniform field and to the linear doublet together is:

$$V = 2M \frac{\cos \theta}{r} - fx \tag{1}$$

But  $x = r \cos \theta$ , so that this equation becomes:

$$V = \left(\frac{2M}{r} - fr\right)\cos\theta\tag{2}$$

If r is the radius of the metal cylinder, this equation expresses the potential of the metal cylinder. But the metal cylinder has zero potential, because we have chosen the y-axis as the region of zero potential in the above discussion. Therefore, V



as given by equation 2 must be zero when r is the radius of the metal cylinder. Therefore the expression in the parenthesis must be equal to zero, or we must have:

$$M = \frac{1}{2} fr^2, \tag{3}$$

which gives the moment of the linear electric doublet to be placed along the axis of the metal cylinder in Fig. 15 to give (when the cylinder is taken away) the field distribution which exists in Fig. 15 in the region outside of the cylinder. The linear doublet is the image in the metal cylinder of the external influence which is the cause of the uniform field in Fig. 15.

It is evident, from Fig. 15. that the presence of the metal cylinder produces a concentration of the electrical stress, the maximum of stress being at the point p. The field intensity at p may be considered in two parts, namely (a) the part -f

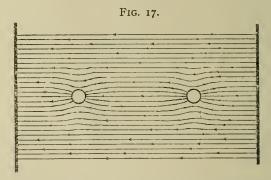
which is associated with the uniform field, and (b) the part which is associated with the linear doublet. This second part is found by taking the value of  $\frac{dV}{dx}$  at p, where V is the potential due to the doublet. But at p (and all along the x-axis) the potential due to the doublet is

$$V = \frac{2M}{x}$$

so that

$$\frac{dV}{dx} = -\frac{2M}{x^2} = -\frac{2M}{r^2}$$

because x = r at p. Substituting the value of M from equation 3, we get -f for the intensity at p of the field due to the doublet. Therefore the total intensity of the field at p is equal to 2f, and



it is, of course, negative, being directed toward the left in Fig. 15.

In the above discussion the radius of the metal cylinder may be anything whatever. Therefore if a wire of any radius is stretched across a region which, but for the presence of the wire, would be a uniform field of intensity f at right angles to the axis of the wire, then the presence of the wire causes a local concentration of electric stress (at the point p in Fig. 15), and the maximum electrical stress thus produced is 2f.

In the case of two ordinary line wires the electrical stress is greatly concentrated near the wires, especially if the wires are small. Indeed, the maximum stress in this case is:

$$f_{max} = \frac{E}{2R \log_e \left(\frac{D}{R}\right)}$$

where R is the radius of the wires, D is their distance apart centre to centre, and E is the voltage between the wires. Now this maximum stress may be very large indeed for given values of E and D, but the maximum stress is reduced to  $2 \times \frac{E}{D}$  by superposing a uniform field of intensity  $\frac{E}{D}$  as indicated in Fig. 17. This exemplifies Fortescue's method of doing away with excessive concentrations of stress by the superposition of a uniform field.

#### THE WORD POTENTIAL AN OBSESSION.

One reason why Mr. Fortescue's paper is difficult to read and understand is that he follows the common practice in making almost exclusive use of the idea of *potential*, whereas the ideas of *field strength* and *lines of force* are more distinctly physical, and therefore more clearly intelligible in verbal discussions. The idea of potential is useful only when one is ready to proceed to the actual mathematical formulation of a problem.

The idea of potential may be most simply exemplified by considering the uniform field as represented by the coarse lines of force in Fig. 12. If this field has an intensity of f volts per centimetre everywhere, and if the upper disk dd is at zero "volts," it follows that the "volts" at a point p which is at a distance of (l-y) centimetres from dd is f(l-y). Now, no doubt, the great majority of electrical men are shocked when one speaks of the "volts" at a point; and, of course, physically speaking, there is no such thing; and yet electrical men speak glibly of the "potential" at a point.

The electric potential at a point is the "height" at that point of an imagined "hill" whose "slope" is everywhere equal to

the electric field intensity.

Some electric field distributions can be looked upon as *slopes* or *gradients*, and such electric field distributions have potential.

Some electric field distributions cannot be looked upon as *slopes* or *gradients*, and such electric field distributions do not have potential.

It is of the utmost importance, especially in discussions leading up to mathematical formulations, to use ideas which have direct connection with physical conditions and things. Thus every one realizes the importance of such ideas as the tempera-

ture at a point, the temperature gradient at a point, the pressure at a point in a fluid, the energy density at a point in an electric field, the velocity of a fluid at a point, the intensity of an electric field at a point, and so on. And we believe with Heaviside that even the correct use of the word potential tends to turn one's attention away from physical things. Every one, and especially those whose ideas are mere thought-habits, will admit the fictitious character of the velocity potential of a fluid, namely, the "height" at a point of an imagined "hill" whose "slope" is everywhere equal to the fluid velocity; but with electrical potential it is different! The word potential (we say the word because very few indeed use the idea) has become an obsession. The magic word energy appears in one of the legitimate definitions of potential, and that settles the matter! Energy, "the only real thing in the universe," as one teacher exclaims! Let us cease talking energy and talk sense, and above all let us keep clear of such blunders as to say "Electric potential may be defined as the condition at a point in space which determines the direction in which an electrified body placed at that point would tend to move." One might as well say that the height of a hill at a place is the condition which determines the direction in which water will flow at that place. The fact is that 99 per cent. of those who use the word potential do not think of potential at all; they think of a vague-composite-offield-intensity-and-energy-and-other-things - too - indefinite - tospecify. The generalized ideas of height and slope have never entered their heads. They do not know that potential is related to electric field as slope is related to height of a hill; and they do not know that the idea of potential is helpful only when one is concerned very particularly with the mode of distribution of an electric field in space.

Decomposition Constant of Polonium. E. v. Schweidler. (Verh. Deutsch. Phys. Ges., xiv, 536.)—The half-time period of polonium was determined quite accurately by means of experiments extending over several years, thus reducing the sources of error. The value obtained was  $136.5 \pm 0.3$  days, which is in close agreement with Regener's value of  $136.0 \pm 0.5$  days. The activity of the preparation was determined by a direct galvanometric and by an electrometric method.

# THE PHYSICAL LABORATORY OF THE NATIONAL ELECTRIC LAMP ASSOCIATION.

A Resume of the Activities of the Laboratory in the Development of the Modern Science of Illumination\*

BY

### EDWARD P. HYDE, Ph.D.,

Director of the Laboratory, Member of the Institute.

The rapid, unparalleled development of the science and art of illuminating engineering is in itself an unanswerable argument for the necessity and value of this, the most modern of the engineering professions. Seven years ago illuminating engineering was but a name known to a few enthusiasts who foresaw the wonderful possibilities in the development of the science of illumination and in the application of that science to the design of illumination installations. The Illuminating Engineering Society of the United States was organized in the early part of the year 1906, and the total number of charter members amounted to only 89.

Now, seven years later, the society has an enrolment of 1400 members, scattered throughout the United States, with a few in Europe, and among its members are to be found physicists, physiologists, psychologists, ophthalmologists, architects, decorators, and representatives of other professions, in addition to those engineers who either directly or indirectly are interested in the application of lighting. On its committees are men of international reputation who are giving their efforts to the development of the science of lighting and to the spread of the gospel of good illumination. The initiative in the movement which resulted in the adoption of a common unit of candle-power for the photometry of gas and electric lamps in this country and in an international agreement on a common unit of candle-power for England, France, and the United States was taken by the Committee on Nomenclature and Standards of

<sup>\*</sup> Presented at the meeting of the Section of Physics and Chemistry, held Thursday. January 30, 1913.

the Illuminating Engineering Society. The inauguration of the course of lectures on illuminating engineering which were delivered at the Johns Hopkins University in the fall of 1910, and which consisted of 35 lectures, delivered by 23 different lecturers, each of whom is an authority in the branch on which he lectured, is to be ascribed to the initiative of the Illuminating Engineering Society. The co-operation with the New York State Board of Factory Inspection in the formulation of bills for legislative enactment in the matter of factory lighting, the stimulation of co-operation with other technical societies through the establishment of reciprocal relations, and the suggestion of an international system of nomenclature and standards in illuminating engineering,—all these and other, activities of the Illuminating Engineering Society are unmistakable evidence of the earnestness and enthusiasm of members of the society, and indicate in a small way the magnitude of the almost unlimited field of activity which should develop in the performance of its legitimate functions.

Illuminating engineering as a distinct engineering profession had its origin in the United States, and has attained to the highest development in this country. The science and art of illumination are now, however, appreciated throughout the civilized world. Four years ago an illuminating engineering society was formed in England, and since its inception this society has done much toward the development of the principles of illuminating engineering and toward the propagation of those established principles. In the past year representatives of the Verein von Gas und Wasserfachmännern and of the Elektrotechnische Verein in Germany have united in requesting the Reichsanstalt to take the initiative in the organization of a German illuminating engineering society. These requests have resulted in the organization of such a society in Germany. There are other important indications of the growing appreciation of the necessity and value of illuminating engineering which might be cited, but they are unnecessary. The experimental stage has been passed, and we all recognize now the raison d'être of illuminating engineering and look to it for results comparable with the opportunities which stretch out before it.

Illuminating engineering is a modern science and art, and yet its principles rest on the correlation, after a new scheme, of the scattered phenomena of the ancient sciences of physics, physiology, and psychology, and the dicta of the ancient art of architecture. In building up and developing the scientific principles of illuminating engineering, therefore, we are forced continually to draw upon the scientific development of the past as recorded in the scientific literature. Many investigators in many different laboratories have contributed to the establishment of the basic principles of illuminating engineering, and have made it possible that application in the art of illuminating engineering should begin contemporaneously with the organization of these scattered principles in the new science of illuminating engineering.

The success of this new science, and therefore of this new art, will depend upon the establishment of sound basic principles. Hence it is of paramount importance that we give our constant attention to the development of the principles of the science, lest its vitality be sapped by the injudicious application of unwarranted assumptions.

One of the many active forces at work at the present time in developing those correlated sciences which form the scientific basis of illuminating engineering is the Physical Laboratory of the National Electric Lamp Association. Four years ago, when the laboratory was in many respects more anticipated than real, a brief description of its purposes and objects was presented before the Illuminating Engineering Society. It may, therefore, be of some interest now, after almost four years of active work, to describe again the equipment of the Physical Laboratory of the National Electric Lamp Association and to present a résumé of the activities of the Laboratory in the development of the modern science of illumination. The purposes and objects of the laboratory are so intimately associated with the development of the basic scientific principles of illuminating engineering that it may well have been called the Illuminating Engineering Research Laboratory. In order, however, to emphasize its purpose of developing the pure science rather than the applied art of illuminating engineering, and to distinguish it from the many other research laboratories which have for their object the technical development and improvement of some commercial commodity, it has been called simply the Physical Laboratory. But, although for simplicity it has been given this name, its functions are not confined to physics. As we shall see later, some of the most

important problems investigated lie in the domain of physiology

and physiological optics.

The Physical Laboratory had its inception in the spring of 1908, when an invitation from the Advisory Board of the National Electric Lamp Association to organize a laboratory for the study of the sciences on which lighting depends was accepted by the writer. In the fall of the same year the duties of the office were entered upon and plans were initiated for the organization of the work. The first year was occupied in supplying suitable quarters and facilities for the work and in selecting a suitable staff of collaborators and assistants. The building which was remodelled to become the first home of the laboratory is that in which Mr. Charles F. Brush developed many of his inventions. In some respects it is well adapted for physical research, but its close proximity to railroad tracks, with the resultant magnetic (and particularly the resultant mechanical) disturbances, renders it entirely unsuitable for radiation and other work requiring the use of sensitive galvanometers and similar instruments. We are now looking forward with keen pleasure to the occupancy, in the near future, of the new laboratory building which is being constructed in the suburbs of Cleveland.

The new building, which has been designed to meet the special requirements of the Physical Laboratory, is a two-story-and-basement structure, 128 feet long and, on the average, 38 feet wide.

As the building will not be entirely ready for occupancy for several months it probably would be premature to attempt to describe it in detail at this time. I might say that each room of the laboratory will be supplied with hot and cold water, gas, pressure, vacuum and a switchboard giving connections to storage batteries and direct- and alternating-current machines in order to get whatever electrical power supply may be necessary. In addition to the office and laboratory rooms, one large and attractive room has been set aside for the library which is being developed. The laboratory subscribes to 97 scientific and technical journals each year, and in addition has accumulated a large number of back volumes of the scientific and technical journals and a number of text-books on subjects of interest to the members of the laboratory and to those in the other departments of the association. The new Physical Laboratory building is heated

by hot-water heat, but as all the windows are double, in order to maintain constant temperature conditions, artificial ventilation is provided. With the view to avoiding any unnecessary vibration in the main laboratory building, the ventilating plant is placed in a small room separate from the laboratory building but connected with it by an underground tunnel. In this room is placed an air-washing system, with heating and tempering coils and blowers in order to supply warm, fresh air to the various rooms of the laboratory.

The instrument shop—a necessary adjunct to a physical research laboratory—is located in the basement of an adjoining building, connected by an underground tunnel with the ventilating plant room and with the main laboratory building. Adjacent to the instrument shop in the same basement are located the storage battery room and the power room. Electric power is supplied by the local lighting power company on a system of 440 volts, 3-phase, 60 cycles, which by the use of suitable motor generator sets is transformed into direct current for charging the storage battery and supplying other necessary power to the laboratory, and into alternating current of various frequencies and voltages for experimental use.

The personnel of the laboratory consists at present of the following:

Edw. P. Hyde, Ph.D., Director.
Francis E. Cady, B.S., Assistant to the Director.
Percy W. Cobb, A.B., M.D., Physiologist.
Charles F. Lorenz, Ph.D., Associate Physicist.
A. G. Worthing, Ph.D., Associate Physicist.
M. Luckiesh, A.M., Assistant Physicist.
H. M. Johnson, Ph.D., Assistant Psychologist.
(Vacant), Assistant Physicist.
One mechanician.
Two stenographers.
Three laboratory apprentices.
A total of fourteen persons.

The equipment of the laboratory, though not extravagant, is ample for all needs, and new apparatus is added from time to time as it is required for the proper conduct of the work of the laboratory. The instrument shop, in charge of a mechanician

of excellent training, is equipped with modern machines, all directly connected and electrically driven.

With this description of the personnel and physical equipment of the laboratory as an introduction, let us turn to the scientific work of the laboratory. It is perhaps not unnecessary repetition to state once again that the Physical Laboratory was organized primarily not for the development of the electric lamp, but for the development of the science of lighting, particularly those branches of the science of lighting which have, or may ultimately have, some bearing on the question of practical illumination. Some unimaginative persons find it difficult to understand why a commercial corporation should engage in what they term a philanthropic enterprise. To those nearsighted and unimaginative persons I would point out that, as in art and in science, so in business, the establishment and maintenance of high ideals is one of the necessary corollaries of complete and continued success.

The industry of incandescent lamp manufacture and the development of the uses of the incandescent lamp in illumination rest on the scientific development of the past generations. It is now a generally-recognized principle in modern business organization to establish a research laboratory for the development of the commercial commodity which is manufactured. But why is it not of equal, if of less immediate, importance to develop the pure sciences from which the practical industrial application must ultimately come? It has been said that inventions flourish best in an atmosphere that is dense with scientific research, and this, I think, is true of an organization as it is of a race.

The organization and development of the laboratory has, therefore, proceeded with this thought in mind: to extend our knowledge in the physics, physiology, and psychology of light, particularly in those phases of these sciences which pertain to the science of illumination. The fundamental idea which has prevailed is the proper co-ordination of physics, physiology, and psychology—the proper co-operation of the physicist, the physiologist, and the psychologist. The work of Helmholtz attests to the accomplishments of a proper co-ordination of physics and physiology. Unfortunately there was but one Helmholtz. Moreover, the domains of the widely-extended sciences of physics and physiology are ever broadening, and the possibility of the

happy combination of the physicist and the physiologist in one man is ever diminishing. The differentiation of the sciences must be accompanied by a co-operation of the scientists if the great middle fields of science are to be adequately covered.

The scheme of organization of the Physical Laboratory contemplates no sharp distinctions among the different divisions of the work, but the problems to be investigated group themselves roughly into three classes: (1) those which have to do with the production of luminous energy; (2) those which have to do with the utilization of luminous energy; and (3) those which have to do with the effects of luminous and attendant radiation. Under the first class comes the investigation of the laws of radiation and of the radiating properties of matter. The problems in this class are purely physical. Much progress has been made in the study of the phenomena and laws of radiation, but our knowledge in this field is still very meagre. Certain simple laws for the ideal complete radiator have been deduced as the result of theoretical and experimental investigation, but the values of the constants appearing in the corresponding equations are in many cases still in doubt, and even the form of the equation is not always agreed upon. Our knowledge of the deviation from the laws of the black body in the radiation of material substances is of most limited extent. The classification of matter on the basis of its radiating properties and the correlation of these properties with the other characteristic properties of matter have scarcely been attempted. Such a classification would be of the greatest scientific interest, and would be of invaluable benefit in the further development of the art of illumination.

Under the third class comes the investigation of the effects of light and of the attendant radiation on the eye, on the skin, and on microscopic organisms, and of those more subtle but equally important effects of light on our mental phenomena, such as attention, memory, and the emotions. Problems in this class are physiological and psychological. The corresponding division is under the charge of a well-trained experimental physiologist, with the assistance of a trained psychologist. The possibilities in this field of work are unlimited, but the obstacles in the way of conclusive results, particularly of the effect of light on the eye and on our mental phenomena, are unusually great, owing to the inherent difficulties in the experiment. Many of the

problems in this field, however, are rapidly being recognized the world over as vital to the welfare of the race.

Intermediate between these two classes of problems—those having to do with the physical production of radiation on the one hand, and those having to do with the physiological and psychological effects on the other—which are distinctly different, there is another which forms the connecting link. The problems of this class have to do with the absorbing, reflecting, and diffusing properties of matter, the measurement of light, i.e., photometry, and the study of the complex phenomena of color and color sensation. The division of the work having to do with the study of these problems comes into closest contact with the actual problems in illuminating engineering practice. It serves as a medium by means of which the scientific results of the other divisions of the laboratory are correlated and applied in a scientific way to practical conditions. As stated previously, the organization of the work into these three divisions does not contemplate sharp lines of demarcation between them, but is intended to insure attention to all phases of the problem before us in order that the concomitant development of the different lines of investigation may conduce to the most valuable integral results.

The scheme of work for the laboratory was developed at the time of its inception, and now, some four years later, we look back over the results accomplished by the laboratory and measure these accomplishments against the standards set at the beginning. It should be remembered that, although the laboratory formally came into existence four years ago last October, the entire first year was consumed in securing laboratory facilities, apparatus, and collaborators. The larger portion of the succeeding year was required for the preparation and development of plans of work, so that the actual scientific work of the laboratory can be said to have begun in the early part of the year 1910, giving thus a period of about three years over which the scientific investigations have extended.

It will be helpful, in reviewing the work of the laboratory, to refer at this point to the first issue of the laboratory publication, which has been termed the *Abstract-Bulletin*. It has been the policy of the laboratory to present the results of the investigations carried out in the laboratory before the scientific and technical societies of this country, and to publish the finished papers in the

recognized scientific and technical journals of the United States and Europe. This has been done because it has seemed unwise to restrict the publications of these investigations to a new journal issued by the laboratory. The introduction of such a new journal would add one other to the already long list of scientific journals which must be subscribed for and read, and, even though there was a willingness on the part of scientific workers to add a new journal to those which they already must review, which is not the case, it would still be difficult to bring the results of the work of the laboratory before all who may be interested, because of the difficulty in securing a circulation comparable with that which has been developed gradually for many of the scientific journals now recognized and subscribed for throughout the civilized world.

But according to this plan of publication the results of the laboratory are distributed in scattered papers in many different journals, and, as it has seemed advisable that the complete work of the laboratory should be collated in such a way as to render it available to all who may be interested, the present Abstract-Bulletin is being published and distributed. This Abstract-Bulletin contains an abstract of every research carried out in the laboratory from its inception to the summer of 1912. The abstracts, written by the authors of the original papers, are fully illustrated with photographs and drawings, in the hope that to all except those who are especially interested in the details of the investigation they may be satisfactory substitutes for the original papers. If then, as a guide, we refer to the Abstract-Bulletin which contains results of all of the scientific work carried out in the laboratory up to the summer of 1912, it will only be necessary to add those investigations which may have been completed in the last six months in order to give a complete survey of the scientific activities of the laboratory in so far as they are concerned with original investigations.

By reference to the Table of Contents of the Abstract-Bulletin we find that 28 papers are abstracted in the first issue of the Bulletin. Of these 28 papers it will be found that nine or ten, or practically one-third of the total number of papers published, have to do with what has been termed the "physical production of light." Three or four papers have to do with the effects of light, and the remainder of the papers, or about one-

half of the total number published, have to do with problems in that intermediate field including photometry and physical questions in illuminating engineering. One problem of considerable interest and importance is the determination of the radiation from metals as a function of temperature. The question arises as to whether the radiation from tungsten or tantalum conforms, in its distribution in the spectrum, to that of a black body at the same temperature, or whether it shows a selectivity in favor of the visible spectrum. In other words, is the efficiency of the tungsten lamp entirely ascribable to its temperature of operation, or is it partially ascribable to a selectivity in its radiation?

The physics of the electric incandescent lamp furnishes an excellent field for investigation and is a logical point at which to begin an investigation of the radiating properties of matter. because of the simplicity of the problem compared with the more complex problem of the physics of the incandescent mantel. Inasmuch as the filament is operated electrically and there is very little, if any, interaction between the filament and the extremely small quantity of surrounding gas, it is much easier by measuring the electric power supplied to determine the total radiation from the filament. This latter question is one which has caused considerable difficulty, but which has been solved in the laboratory, the results of the investigation of this problem being published under the title "A Study of the Energy Losses in Electric Incandescent Lamps." It is very helpful, in studying the radiation of metals, to be able to measure accurately and easily the total energy radiated. This is very difficult to determine by any objective absolute method, but i comparatively simple of determination if we know the correction to be applied to the power supplied to a filament. We know that the total energy supplied to a filament is radiated except in so far as there is some loss by thermal conduction at the leading-in and anchoring wires. A method has been developed in the laboratory by which it is possible to determine accurately the amount of energy supplied per second to each element of length of the filament, the amount of energy radiated by each element of the filament, and the luminous value of the radiation from each element of the filament. In this way it is an easy matter to determine, from the energy supplied, the total radiation, applying a correction for the ends of the filament.

This study of the energy losses in electric lamps must be considered as auxiliary to the main problem in hand. In addition to the investigation of this problem, another auxiliary problem presented itself for investigation, viz., the determination of the correction which must be applied in spectro-photometric measurements owing to the impurity of the spectrum. It is known that if two continuous spectra, somewhat different in energy distribution, are intercompared by means of a spectrophotometer, the ratios obtained from the spectro-photometric settings do not represent accurately the relative distribution of energy in the two spectra, but that a correction must be applied. This problem has been investigated in the Physical Laboratory with considerable thoroughness from the theoretical standpoint, and the results have been tested and verified by experiment. In connection with this latter investigation a new form of variable rotating sectored disk for use with the spectro-photometer has been developed, and has been shown to be very satisfactory in actual operation.

Having completed these auxiliary investigations, attention was turned again to the main problem,—namely, that of the investigation of the radiating properties of matter—and a new determination was made of the selective radiation from tantalum. During the past year much work has been done on the radiation from metals following the line of attack initiated by the writer. The results of this work have been correlated and published in a paper entitled "The Synthetic Development of the Radiation Laws for Metals." As stated before, it must be remembered that the investigation of the radiating properties of matter was begun at the simplest point of attack—namely, with filaments of metal mounted in exhausted bulbs. It is the intention, however, to continue this work to the investigation of the radiating properties of other materials, such as the rare earth oxides as found in the incandescent mantle. The difficulties to be encountered in this work will be very much greater than those encountered in the study of the radiating properties of metals.

It is interesting to digress here from the consideration of papers abstracted in the *Abstract-Bulletin* to refer to some work that has recently been done, largely in continuation of the method used in studying energy losses in electric incandescent lamps. It was noticed by Dr. Worthing that the distribution of tempera-

Vol. CLXXVI, No. 1051-7

ture along the two legs of a filament with respect to a point of support was different, and that the difference depended on the direction in which the current was flowing through the filament. By accurate measurement of these differences it has been found possible, through the use of a formula developed theoretically, to measure the Thomson electromotive force in metals at high temperatures, as these differences in distribution of temperature on the two sides of the anchor or support are unquestionably due to the operation of the Thomson electromotive force on one side in conjunction with, and on the other side in opposition to, the electric current. This investigation has been completed and the results have been published in abstract. The complete paper is now ready for publication, although no reference is made to it in the *Abstract-Bulletin*.

Another investigation which was carried out by Dr. Worthing, using in part the method which was used in studying the energy losses, was the study of Lambert's cosine law of emission for tungsten and carbon. It can readily be shown theoretically that for a black body the radiation emitted by a cm.2 of surface at any angle is equal to the radiation emitted normally, multiplied by the cosine of the angle between the normal direction and the direction in which the observation is made. It has usually been considered that for most ordinary substances the radiation at any angle is less than that computed on the basis of Lambert's cosine law. As the result of an investigation of this question by the new method Dr. Worthing has shown that in the case of carbon the deviation is in the ordinarily-accepted direction, but that in the case of tungsten the energy emitted at any angle up to 80 degrees or 85 degrees is larger than that which should be emitted on the basis of Lambert's law. A careful study showed that this deviation for tungsten increases from an angle slightly different from that of normal emission to an angle of 70 degrees or 75 degrees, where the deviation becomes as large as 15 per cent. Beyond this angle the emission falls off, and beyond 80 degrees or 85 degrees the deviation is in the direction ordinarily considered to hold, and which was found to hold uniformly for carbon. This investigation was completed some months ago, and has just appeared in the Astrophysical Journal, but it is not referred to in the Abstract-Bulletin.

Returning to the papers abstracted in the Abstract-Bulletin

and having to do with the production of light, one very important and thorough piece of work carried out by Dr. Ives and Mr. Luckiesh has been published under the title "The Effect of Red and Infra-red on the Decay of Phosphorescence in Zinc Sulphide." This investigation brings out some very interesting results on the relation between the time of decay and the shape of the decay curve in its relation to the effect of red and infra-red excitation. In addition to these more important lines of work on the physics of light production, one or two other pieces of investigation, such as a further study of the radiation from the firefly and the study of the ultra-violet radiation from common illuminants, have been carried out.

Passing now to the investigations having to do with the effects of luminous and attendant radiation, we find that the published papers on these subjects are not as numerous as those on some of the other more physical phases of the question. The reason for this is twofold. In the first place, it is necessary to spend more time in developing methods in this field of research, as the point of departure is new. In the second place, the organization of this division of the work has not been developed as rapidly as that of the other divisions. The investigation by Dr. Cobb on "The Influence of Illumination of the Eye on Visual Acuity" is to be mentioned. Another investigation bearing on a similar question by Mr. Luckiesh, of which mention should be made, is the investigation of "The Dependence of Visual Acuity on the Wavelength of Light." The problem of so-called "glare" is one of very great importance and interest, but it is one of great difficulty. The investigations by Dr. Cobb and Mr. Luckiesh on this subject constitute a beginning. Though not mentioned in the Bulletin, much more work has been done on this subject. Dr. Cobb, in conjunction with Dr. Geissler, formerly the psychologist of the laboratory, has carried out an elaborate investigation of the influence of the visual field on acuity and on the determination of the least perceptible difference. The results of this investiga-tion have been presented recently before the American Association for the Advancement of Science, and will soon, I hope, be published in full. It is the intention to begin in the very near future an investigation which will have for its object the determination of the possible influence of glare,—i.e., of an extraneous bright light in the field of view, on the muscular

control of the eye, on the nervous system, on circulation, and on other physiological processes subject to measurement,—in the hope of finding some immediate definite symptom of the deleterious effect of glaring light sources in the field of view. Other problems in physiological optics have been begun and are in part finished, but are not yet ready for presentation.

By far the largest number of papers abstracted in the *Bulletin* have to do with problems in that intermediate field more closely connected with the direct application in illumination. Especial attention is to be called to the classical work of Dr. Ives and Mr. Luckiesh on heterochromatic photometry and on the study of color. The limitation of time precludes the possibility of doing more than mentioning the titles of a few of these pieces of investigation to give one an idea of the extent and diversity of the problems investigated in this field. Among these may be memtioned: "Studies in the Photometry of Lights of Different Colors," "Note on Crova's Method of Heterochromatic Photometry," "Color Measurements of Illuminants—A *Résumé*," "Effect of Yellow Glass on the Efficiency of Incandescent Lamps," "Subtractive Production of Artificial Daylight."

It may be a matter of some historical interest to record here. what, so far as I know, was the beginning of the investigation of color in artificial illumination, other than in the more or less academic way of determining the distribution of energy in the visible spectra of light sources, such as has been done, of course, for very many years. The first investigation of color in illumination was undertaken in connection with a test which was made on the installation of Moore tubes in the New York Post Office by the Photometric Section of the Bureau of Standards in June, 1908. A short time previous to this Mr. F. E. Ives had placed on the market his colorimeter, designed principally for determining the color of fabrics, papers, etc. In connection with the other tests which were made on the Moore tube in comparison with other installations it was suggested that a determination of the color value would be of interest, and an invitation extended to Mr. F. E. Ives to make such a test with his colorimeter was accepted. Unfortunately, owing to conditions more or less beyond our control, the results of this test were of very little direct value, but the indirect value has been accumulating ever since that time. Shortly afterwards Mr. Ives made more accurate

color measurements on the Moore tube, and subsequently Dr. Ives, at the Bureau of Standards, in connection with the work in photometry, undertook measurements on the Moore tube and on other light sources. Since that time numerous investigations have been made on color in artificial illumination, and at the present time this is one of the important elements which are taken into consideration in illumination installations and in tests made on such installations.

It is, of course, impossible in a limited time to review even in moderate detail the research work accomplished in the laboratory. Moreover, neither does time permit nor is this the place to discuss at length the activities of the laboratory in connection with the various engineering societies, the co-operation with which has been considered one of the valuable functions which the laboratory should perform.

In closing it may not be amiss to refer briefly to some of the plans of the laboratory for the future. First, it should be stated that there is no intention of altering seriously the general plan of organization that has been developed. On the other hand, it is hoped that this plan may develop still further, and that through co-operation more and more of the important problems which are on the border-line between physics, physiology, and psychology may be attacked and important results may be obtained. The physical work is fairly well organized at the present time, but even in this field the laboratory has been handicapped, owing to the lack of steady conditions for accurate sensitive galvanometer measurements, such as we hope to have available in the new laboratory. There is a vast field for investigation in the physiology and psychology of light—a field which has only been touched at the border. It is hoped that in this important line of research some of the difficulties will be overcome and methods will be developed which will yield results of some definite value.

The Physical Laboratory of the National Electric Lamp Association occupies a unique position among the laboratories of the world, and it is the hope and desire of those responsible for it and of all those associated with it that the laboratory may be made as useful as possible in developing the science of light in its relation to the science of lighting. To this end we are ever awake to suggestions that may enhance the value of its contributions. One plan which is at present under consideration is that of

possibly opening the doors of the laboratory to a limited number of advanced students and members of university faculties to undertake research work on subjects correlated with those in which the laboratory is interested and under conditions most favorable for those investigations. It is thus hoped that it may be possible to open a few rooms in the laboratory to advanced students in physics who desire to carry out research work under conditions where the value of the application in the industries is appreciated, so that the laboratory may partially assist in supplying a want which would seem to exist at the present time. There seems to be no reason why there should not be as great a demand for physicists in the industries as there is for chemists, and I am of the opinion that this is due, at least partially, to the lack of development of physicists appreciative of the atmosphere which prevails in industrial work.

In a somewhat similar way, if I am correctly informed, there is need of research work by ophthalmologists on questions pertaining to the relation of light and other radiations on vision. I am told that very little research work in ophthalmology is being done in this country, and that that which is being done is confined principally to the pathology of the eye. It has been suggested to me that possibly it might be of value to open a room of the laboratory for an investigator in some problems that are ophthalmological in their results but which require physical and physiological apparatus and facilities in order to be properly carried out. In every department of the laboratory's activities we would be grateful for suggestions and criticisms in order that the laboratory may fulfil its mission to the highest possible degree.

As has been said, the principal object of the Physical Laboratory of the National Electric Lamp Association is not invention or the development of the electric incandescent lamp, but rather the development of the science of light in its relation to the science of illumination. It is, however, the hope and expectation of some of us connected with this laboratory that there may grow up and develop, co-ordinate with but distinct from the division for pure research, a separate division on industrial physics which shall be organized primarily for the practical development of illumination methods and of the incandescent lamp. There would then be in one organization the complete cycle of activity, beginning with the development of pure science

and ending with the sale of a commercial commodity. The motto of the Physical Laboratory, inscribed over the portal of the new building, is "Veritas vos Liberabit," but in order that the truth shall make us free it is necessary that the truth shall be propagated and that the truth shall be applied.

It seems peculiarly fitting to-night, in this Institute founded as an appropriate memorial to that illustrious scientist, who at the same time was keenly appreciative of the application of science in the arts, that here to-night I should present to the members and friends of the Franklin Institute the results, meagre though they be, of the first laboratory in the world, so far as I know, organized and supported by a commercial organization for the development of pure science. If Benjamin Franklin were here to-night I am sure that his heart would glow with joy and satisfaction at the thought that the United States was fulfilling in the most complete and highest sense its destiny as the first industrial nation of the world. Those of us who are responsible for the results accomplished by the Physical Laboratory of the National Electric Lamp Association are keenly appreciative of the unusual responsibility devolving upon us, for in my judgment an element of positive worth in the progress of civilization will have been destroyed if this first experiment is unsuccessful and the principle underlying it is inferred to be fallacious. It is therefore hoped that the friendly criticism and advice of those who are in sympathy with the idea underlying the organization and purpose of the laboratory may be given, to the end that the laboratory may realize its ideals and that the principle of the organization and support by a commercial organization of a laboratory for pure science may be established as sound in theory, practicable in operation, and valuable in results.

Corrosion Test of Monel Metal. Anon. (Foundry, xl, 505.) —The New York Board of Water Supply made corrosion tests on several metals by burying samples in the earth for six months, and periodically wetting the earth with dilute solutions of corrosive salts. The losses were: phosphor bronze 0.09 per cent., Tobin bronze 0.11, monel metal 0.12, manganese bronze 0.12, Muntz metal 0.33, and steel 1.04 per cent. The monel metal made the best appearance of all after the test.

Kambara Earth: A Decolorizing Material for Mineral Oils, Etc. K. Kobayashi. (J. Ind. Eng. Chem., iv, 891.)—Kambara earth is from the Echigo province of Japan and belongs to the same class of fuller's earth as that found in Florida, but is more efficient. It resembles hard wax, feels soapy, has detergent properties, and is dissociated by and miscible with water. It consists of fine particles of earth without any admixture of quartz. Its contents are: silica 60.71 per cent., aluminum oxide 13.18, iron oxide 3.68, calcium oxide 0.62, magnesium oxide 0.38, sodium and potassium oxides 1.54, and loss on ignition 20.04 per cent. It is essentially composed of hydrates of silicic acid and aluminum silicates. Numerous experiments on its action with dyes are recorded. crude petroleums it absorbs the unsaturated hydro-carbons. removes certain impurities from methyl alcohol, and tar from pyroligneous acid. The earth is slightly acid, and is thus distinguished from ordinary kaolin and clay, and probably some of its efficiency is due to this acidity.

Use of Mica as an Insulator. F. Wiggins. (Elec. Rev., lxxi, 564.)—Mica can be obtained in sizes up to 24 inches by 12 inches. The limitations of micanite are pointed out, but the quality depends largely on the price paid. Pure mica tubes, consisting entirely of rolled mica without any cement, can be obtained up to 12 inches or 18 inches in length, and, as they can be used much thinner than the micanite tubes, the increased cost is not so large as might appear at first sight. Hints are given as to the splitting and working of mica, which requires care and experience.

Dangers of Coal. M. Dennstedt and L. Schafer. Angew. Chem., xxv, 2625.)—Commences by describing an apparatus and a method by which coals may be tested and classified as regards their liability to self-ignition. Such tests would furnish definite data as to the safety or danger of storing and transporting any particular type of coals. Coals which when heated to 150° C. in a stream of oxygen show no tendency to increase of temperature are absolutely safe; those which show a slight tendency to heat up locally but fail to ignite within an hour are safe enough for storing and transporting on board ship. Those which ignite within an hour and below 150° C. are relatively dangerous coals. temperature of self-ignition, and the time of heating necessary, determine relatively the degree of danger. In general the heat value of the coal is not an index as to its tendency to self-ignition; brown coals are much more dangerous in this respect than soft coals. The presence of finely-divided particles in a coal pile increase this danger greatly. The coals tested show that the greater the percentage of oxygen in the coal the greater the liability to self-ignition.

#### NOTES FROM THE U.S. BUREAU OF STANDARDS.\*

#### WEIGHTS AND MEASURES CONFERENCE.

Among the important legislation reported upon by the secretary of the recent Weights and Measures Conference at the Bureau of Standards there were two national laws: The first was an act to establish a standard barrel and standard grades for apples when packed in barrels, which was approved August 3, 1912. "This act does not prevent the shipment in interstate commerce of either inferior apples or of apples packed in short barrels if they are not marked so as to bring them under the law. It merely provides that if apples are sold and marked to conform with the regulations of the act, they must be packed in the standard barrel and be of specified quality and size."

The other is an act of far-reaching importance in the amendment to the Food and Drugs Act, which requires that all food for interstate shipment put up in package form must have the net contents plainly and conspicuously marked on the outside of the package in terms of weight, measure, or numerical count, provided that reasonable variations shall be permitted and tolerances and exemptions as to small packages shall be established by rules and regulations made by the Secretary of the Treasury, the Secretary of Agriculture, and the Secretary of Commerce.

A board representing the three Secretaries is at present engaged in drawing up the rules and regulations for the enforcement of this act. This act has wide application in connection with the enforcement of the national Food and Drugs Act and similar acts passed by the various States.

This decision, in substance, is that the States can not adopt regulations which are in conflict with those made or adopted under the authority of Congress.

The activity in the States in regard to weights and measures legislation reported on at the last meeting has been continued this year, the following named States having passed laws on the subject of weights and measures: Arizona, Idaho, Indiana, Louisiana, Maine, Maryland, Massachusetts, Michigan, Minn-

<sup>\*</sup> Communicated by the Bureau.

esota, Nebraska, New Hampshire, New Jersey, New Mexico, New York, Ohio, Oregon, Pennsylvania, South Carolina, Virginia, Vermont, and Washington. Quite a number of other States considered bills, and the prospects are encouraging for considerable progress at the next legislative sessions.

The conference has long been in favor of the passage of a law to establish a standard barrel for all dry commodities shipped from one State to another. Such bill was introduced into Con-

gress at its last session.

## THE TESTING OF CAPACITY MEASURES.\*

# By R. Y. Ferner,

Bureau of Standards.

This paper describes the methods used for determinations of the volume of capacity measures, varying from the precision test of high-grade primary standards for State governments to the rough determinations by linear measurements of the dimensions of the measure. The precision test is applied to measures used as standards by State and city sealers of weights and measures and as master measures in manufacturing plants. The determination is made by weighing the amount of water contained in the measure, and from tables of water weights the correction of the measure is determined. Precautions to be observed in the filling and weighing of the measure are noted, and tables and charts are given for the rapid computation of the results. The method can be used to an accuracy of from one part in 50,000 to one in 100,000. Factors that may be omitted in the application of this method where less accuracy is required are pointed out.

For determinations to an accuracy of from one part in 500 to one in 1000 the method of pouring water from a standard to the measure under test is used, and precautions to be observed in the manipulation are given. For the test of rougher measures, particularly of dry measures which will not hold water, tests are made with seeds as a medium. Results are given of a series of experiments made to determine which kinds of seeds are the best for this purpose. For the smaller measures the small

<sup>\*</sup>A paper read at the Eighth Annual Conference on Weights and Measures, held at the Bureau of Standards, May 14-17, 1913.

spherical seed called rape seed proved to be much better than the commonly used flaxseed, while for larger measures dried peas are recommended. The effects of varying heights of fall of the seed, of shaking down or jarring the seed during the test, and of different methods of striking off the surplus seed are discussed. Results varying from one part in 100 to one in 400 may be obtained by this method. Finally the various gauges on the market for determining the accuracy of measures, particularly dry measures, by measurements of their dimensions are described, and simple formulæ are given for the rapid computation of the volume of measures by the linear dimensions. Results by this method vary in accuracy from 2 per cent, to 0.5 per cent.

#### ELECTROLYTIC CORROSION OF IRON IN SOILS.\*

By Burton McCollum and K. H. Logan.

This is an experimental paper dealing with the fundamental laws governing electrolytic corrosion of iron imbedded in soils. The results are expressed in terms of electrolytic corrosion efficiency. If the corrosion of the anode is the sole reaction involved at the anode, then according to Faradav's law 96,540 coulombs are required to corrode one gramme-equivalent of the metal, and the corrosion efficiency is said to be 100 per cent. In most cases, however, the actual corrosion noted is either greater or less than this amount, and the percentage which the actual corrosion in any case is of the theoretical amount is called the efficiency of electrolytic corrosion. The experimental data presented in the paper show how the efficiency of corrosion is affected by the varying physical conditions encountered in practice. It is found that current density has a marked effect on the efficiency corrosion of iron in soils, the efficiency being in general greater the lower the current density. In saturated soils efficiency of corrosion may vary between 20 per cent., and about 140 per cent., for the range of current densities between 5 milliamperes and .05 milliampere per square centimetre. Moisture content in the soil also has a marked effect on efficiency of corrosion, the corrosion being in general greater with increasing moisture content up to saturation of the soil.

<sup>\*</sup> Technologic Paper No. 25, Bureau of Standards.

Temperature changes within the limits commonly met with in practice, the amounts of oxygen present in the soil, and the depth of burial of pipes below the surface have no material effect on corrosion efficiency. The voltage impressed on the electrodes likewise has no material effect on the corrosion efficiency except in so far as the current density may be affected.

The pitting of iron imbedded in soils is found to be affected not only by a non-homogenous condition of the iron itself, but also by the chemicals contained in the soils; certain chemicals, such as nitrate, for example, give rise to comparatively uniform corrosion, whereas certain others, particularly chlorides, produce

much greater pitting effects.

While it is found that the amount of oxygen present has no appreciable effect on the corrosion efficiency, it does affect in a marked degree the character of the end products formed. If the corrosion is rapid and the supply of oxygen small there will be a preponderance of magnetic oxide, while if the rate of corrosion is slow and the supply of oxygen abundant, the ferric oxide will predominate. Owing to the fact that the supply of oxygen around the pipes buried in earth is always more or less limited the character of the oxides formed gives some indication as to the rate of corrosion, and thus indirectly the cause of the corrosion if local conditions are properly considered.

There is no material difference in the efficiency of corrosion shown by the various kinds of iron commonly used in the manufacture of underground pipes so long as physical conditions are similar. In actual practice, however, wide variations of corrosion in all kinds of iron may be expected, and the results of a large number of tests show that under most practical conditions the corrosion efficiencies will range between 50 and 110 per cent.

The paper also gives a great deal of data on the subject of the resistance of soils and its variation with temperature, moisture content, and other physical conditions, and discusses the relation between these resistance changes and stray current electrolysis.

THE Bureau of Standards will shortly issue the Technologic Paper No. 14 on "Legal Specifications for Illuminating Gas," which is a brief discussion of the recommendations made by this Bureau for State or city laws to control the quality of illuminating gas sold.

The Bureau undertook several years ago an investigation of calorimetric standards and of flame standards for gas photometry, but as the work progressed it became evident that other phases of gas testing were equally deserving of attention, and the field of the investigation was therefore extended to include all

gas-testing work.

As the heating value of a gas is a better measure of its usefulness for power, heating, or lighting with mantles than is the candle-power of the gas, the heat delivered to customers should be measured and controlled in order to insure good service. For open-flame lights only, the candle-power must be maintained. As many persons still use such burners, even though they are less economical than a mantle, the candle-power can not be entirely overlooked. The Bureau of Standards proposes that a secondary requirement be fixed by cities to insure sufficient candle-power of the gas for this use, and that the heating value be made the principal basis of gas rating.

The basis of rating of the gas and its purity are also discussed in this paper. Copies may be had by addressing the Bureau of Standards, Department of Commerce, Washington,

D. C., referring to Technologic Paper No. 14.

# THE FUNCTION OF TIME IN THE VITRIFICATION OF CLAY.

THE Bureau of Standards is sending to press Technologic Paper No. 17 upon the function of time in the vitrification of clay. The paper is a study of six clays which were heated to their maturing temperatures at definite rates and comparing the heat effect by means of porosity and shrinkage determination.

Time is an exceedingly important factor in the maturing of clays and bodies. A certain result may be obtained either by the use of a higher temperature for a shorter time or a lower temperature for a longer time. This fact we see constantly illustrated in the firing of all kinds of clay products, the melting of glass, the softening of pyrometric cones, etc. Yet there are definite thermal limits to which such relations are confined. These correspond to the lowest temperature at which partial softening, which is a necessary condition of vitrification, can take place.

The effect of the time-temperature relations should be studied closely for every clay, since only when reliable information concerning this subject is at hand is it possible to exercise complete control of the burning. The importance of such results applied in factory practice cannot be emphasized too much.

The use of pyrometers in plant operation is to be urged most strongly, as they afford the only means of controlling the rate of firing. For the establishment of the end point of the burned pyrometric cones, shrinkage and porosity determinations are of value.

In the use of cones the time factor should be taken into account.

Wood, Paper, and Steel Pulleys. H. A. Woodworth. (Power, xxxvi, 848.)—Woodworth and E. D. Biggs made tests at Purdue University to determine the breaking strength of pulleys of different materials with the object of ascertaining their principal points of weakness. Mechanical engineers will find these very interesting. Some of the conclusions arrived at are: (1) Rim joints midway between arms are serious defects and materially reduce the bursting speed. (2) The solid-web-and-rim paper flywheel will safely withstand a peripheral speed of 106 feet per second. (3) Wood flywheels with solid rims have an ample factor of safety at a peripheral speed of 90 feet per second, if the wood is of good quality. (4) Steel wheels of the split-rim type are unsafe at speeds above 80 feet per second.

Special Rails for Heavy Curves and Grades of the Lehigh Valley Railroad. Anon. (Eng. News, lxviii, 779.)—The use of specially heavy rails on sharp curves and steep grades, where conditions of rail wear are severe, is being successfully introduced by the Lehigh Valley Railroad. The rail is a 110-pound section of the same height and base width as the 100-pound standard, but with a heavier web, 19/32 inch instead of 9/16 inch; and a larger and much deeper head, 17/8 inches deep instead of 19/16 inches. A six-bolt joint is used, but the outside splice bar is of special design, extending along the side of the rail head to secure additional depth and rigidity. A section of the 110-pound rail and its splice joint, with the head of the 100-pound rail shown in dotted lines, is given. There are at present about 77 miles of track laid with the 110-pound rail, and additional rails in process of laying will bring the total to about 100 miles. A compromise joint is used to connect rails of the two forms of section, the tops being stepped to fit the different heights of web and head.

# THE FRANKLIN INSTITUTE

# AWARD OF THE ELLIOTT CRESSON MEDAL TO DISTINGUISHED SCIENTISTS AND TECHNOLOGISTS.

To the roll of distinguished scientists and technologists who have received from The Franklin Institute its Elliott Cresson Medal—the highest recognition in its gift—have been added\* the names of Lord Rayleigh, Sir William Ramsay, Prof. Dr. Emil Fischer, Dr. Charles P. Steinmetz, and M. Emile Berliner.

Mr. Berliner, Dr. Randolph and Dr. Steinmetz were present at the Stated Meeting of the Institute on the evening of Wednesday, May 21, and received the medals awarded them from the President of the Institute, Dr. Walton Clark.

They were presented by Dr. Harry F. Keller. In presenting Mr. Berliner, Dr. Keller said:

"MR. PRESIDENT: The Committee on Science and the Arts has again assigned to me the most agreeable duty, or rather conferred upon me the privilege, of presenting to you the distinguished scientists and inventors whom The Franklin Institute desires to honor by the award of the highest recognition at its command, the Elliott Cresson Medal, and who are honoring the Institute by personally appearing at this meeting to receive it from your hands.

"A recent writer in one of our scientific magazines, in commenting upon the wonders of the modern world, calls attention to the fact that most of the great inventions and achievements are the results, not of the labors of individuals, but rather of some general element of modern progress. While it cannot be denied that this is true of the majority of scientific discoveries, useful inventions, and engineering feats, it must also be conceded that in nearly every instance the culminating achievement can be connected with one or a few great names.

"Thus one of the most marvellous of modern inventions, the one that received the second largest number of votes in an international ballot on "The Seven Wonders of the Modern World"—I refer to the telephone—was not the practical and useful device it is to-day when it first came from the

<sup>\*</sup> See last issue of this Journal, page 655.

hands of its inventor, but had to be modified and improved by others before it was universally introduced as an indispensable means of communication.

"A year ago The Franklin Institute awarded the Elliott Cresson Medal to Alexander Graham Bell, to whom undoubtedly belongs the honor of having solved the problem of the electrical transmission of articulate sounds, and of constructing the first speaking telephone. But at the very time when the award was made your Committee on Awards was considering the fitness of bestowing a similar recognition upon another pioneer in the transmission of speech and an inventor who more than any other has helped to make Professor Bell's great invention the perfect instrument to which we are accustomed.

"Born and educated in Germany, he came to this country in 1870, and after engaging in mercantile pursuits for several years he devoted his attention to the problems of the electrical transmission of speech. In 1877, the year after Bell had exhibited his telephone at the Centennial Exhibition in this city, he invented the loose-contact transmitter bearing his name, and which brought the telephone within the range of practical use and commercial application. Shortly afterward he effected another great advance in telephony by the use of the induction coil to step-up the low tension variable current through the loose-contact transmitter to a higher tension variable current in order to overcome the impedance of long lines.

"When, in 1878, the Bell Telephone Company was formed, he was appointed chief inspector at its works in Boston, and the first twenty thousand transmitters that went into use passed through his hands. In his capacity and later, as consulting expert to the Bell Telephone Company, he brought out and patented many other inventions relating to the telephone art.

"In the meantime he took up the improvement of the talking machine. In 1887 he invented the gramophone, which was the first talking machine that employed a record with a groove of even depth and varying direction, and in which the groove not only vibrates the recording stylus but also propels it. The device was exhibited by the inventor before The Franklin Institute in 1888, and on its recommendation the John Scott Medal was awarded to him by the city of Philadelphia.

"Under various trade names—the 'Victor' Talking Machine, for instance—the gramophone has achieved universal popularity and become the basis of a great and growing industry. It carries entertainment, instruction, and culture to the homes and the masses of the people of every country and clime, and it has in a very marked degree promoted and spread the appreciation of high-class music.

"Our medallist's inventions have by no means been confined to applications of electricity; he has also made notable and valuable improvements in the construction of motors and other devices used in aëroplanes. In recent years he has given much thought and attention to the pathology of milk, and his educational campaign on this subject has been fruitful of beneficial results in the interest of public hygiene.

The distinguished electrical engineer, the resourceful inventor, and the philanthropist who has accomplished all these things and many more that I cannot enumerate for lack of time, I have the honor to introduce to you, Mr. President, as Mr. Emile Berliner, of Washington, D. C."

In presenting Dr. Randolph:

"MR. PRESIDENT: There is, perhaps, no better proof of the wide usefulness of this Franklin Institute, and of the high esteem in which it is held, than the fact that most of the American recipients of the Elliott Cresson Medal have at one time or another, and in many cases repeatedly, come here to address our meetings, either to exhibit and explain discoveries or inventions they have made, or to discuss those subjects in which they have been particularly interested or active. Thus only recently one of the foremost civil engineers which our country has produced and who is to receive that medal here to-night, addressed us in this hall in a most illuminating and inspiring manner on the theme "The Engineer in the Building of the Republic." address was published in the March number of our Journal, and it so well describes men who, like its author, have had a hand in the building of this Republic of ours, that I feel it would be impossible to introduce him better than by quoting has own eloquent words: 'What manner of man is he? Physically, like King Saul of old, he may stand head and shoulders above the people; he may be a man of brawn and sinew, or he may be frail and dapper, but in either case he will have the gift of continuance; he will set out to reach a goal, and no matter what obstacles lie in his path, he will reach it.

"'He endures hardship like a good soldier; summer's heat and winter's cold try his endurance, but he endures. He traverses rough places of the earth with an assured tread; his path is in the wilderness, and the solitary places know his footfall. If hunger overtakes him, he tightens his belt and still endures; thirst parches his tongue, but there are water springs, and he endures until their cooling draughts refresh him. The physical man is dominated by the intellectuality which dwells within him. Engineering is a science far-reaching and many-sided, dealing with the forces of Nature in all their varied forms and combinations. This man of whom we are talking, perhaps—we may say assuredly—has not mastered this science in all its branches, but he has chosen the division of that science to which he will devote his energies, physical and mental and that he knows. He may have acquired that knowledge within college walls, and his alma mater may be dear to him, or he may have acquired what he knows in the hard school of experience, ending up days of toil with nights of study, that he may know the reason for the things he has been doing or be ready to meet the problems that he knows lie ahead of him. He has more or less of the constructive instinct. He is a dreamer who can shut his eyes and see the things he means to create take outline and form upon the trestle-board of the imagination. Or he maps in relief the territory over which he has tramped and selects upon the wrinkled face of Nature those furrows through which he will carry the roadway, excavate his canal, or across which he will build his dam.' Such is the man whose great and brilliant achievements in engineering The Franklin

Vol. CLXXVI, No. 1051-8

Institute desires to crown with its highest award. Born at New Market, Virginia, he acquired his education 'in the hard school of experience.' At the age of 20 he entered the service of the Baltimore & Ohio Railroad, and, rapidly advancing in his profession, he for many years devoted his energies to railroad engineering, acquiring a most varied and extended experience in the building of roads, freight-houses, and terminals. Since 1886 he has been engaged in general engineering work, and he has served as consulting and directing engineer in the carrying out of many projects of the first magnitude. Among these should be especially mentioned the construction of the great Sanitary and Ship Canal for the city of Chicago, his service under President Roosevelt on the Board of Consulting Engineers for the Panama Canal, the harbor improvements of Milwaukee, and the planning of the Deep Waterway from Lockport to Utica, but to enumerate all, even of his more important achievements, would take up much more time than is allotted to me.

"Mr. President, I have the honor to present to you Dr. Isham Randolph,

of Chicago."

#### In presenting Dr. Steinmetz:

"MR. PRESIDENT: Last but not least of the trio of intellectual giants whom to pay homage to we have gathered here to-night is a man whose great achievements may not appeal to the popular understanding to the same extent as do those of the other two medallists. His name is not associated with any popular inventions or mentioned as that of the originator of great engineering feats; nevertheless, his wonderful intellect and ability have made him a leader in the development of that most useful of the wonders of the modern world, electricity. His chosen field is the mathematics and theory of electricity, and there is probably no branch of human activity in which mathematics—the higher mathematics-and theory have a more direct bearing upon practical results than in electrical engineering. Like his confrère, Mr. Berliner, he was born and educated in Germany. He received his training in the sciences and in mechanical engineering at the University of Breslau and the Zurich Polytechnikum; but his practical experience and a field for exercising his extraordinary abilities he found in our country, to which he came at the age of 24. The biographical sketch prepared by the Committee of Awards does not indicate that his life here has been an eventful one in the accepted sense of the term. His first position in this country was that of a draughtsman with the Eickemeyer Manufacturing Company, in whose employ he remained as electrical engineer and constructor, and then as Director of its Research Laboratory, until the Eickemeyer interests were absorbed by the General Electric Company, when he accepted a position in the calculating department of this largest corporation of its kind. When the headquarters of the company were transferred from Lynn, Mass., to Schenectady, N. Y., in 1894, he was given charge of the calculation and design of the company's apparatus, as well as of the research and development work. In 1902 he was called to

the chair of Electrical Engineering in Union University, still retaining, however, his connection with the General Electric Company as consulting engineer. In 1911 he organized and assumed charge of its Consulting Electrical Department.

"His constructive work has greatly advanced the electrical art, and special mention must be made of his improvements in alternating current

motors, generators, converters, regulators and lighting.

"He has written a great number of books, papers, and addresses upon mathematical, engineering, and scientific subjects. His text-books and treatises are recognized as standard works, and his papers embody the results of the profoundest study and reasoning. Two years ago he stood before an audience in this venerable hall and conducted his listeners into "Some Unexplored Fields of Electrical Engineering."

"We may rest assured that such fields cannot long remain unexplored when they are entered by so penetrating, brilliant, and disciplined a mind as that of this investigator, Dr. Charles Proteus Steinmetz."

Brief biographical sketches of this year's recipients of the Elliott Cresson Medal are given below.

#### LORD RAYLEIGH, J.P., D.C.L., LL.D., F.R.S., Hon. C.E., Sc.D.

JOHN WILLIAM STRUTT, third Baron Rayleigh, was born in Essex on November 12, 1842. He was educated at Trinity College, Cambridge, from which he was graduated as senior wrangler in 1865, obtaining the first Smith's prize of the year.

From 1879 to 1884 he was Cavendish Professor of Experimental Physics at the University of Cambridge; and in 1887 he accepted the post of professor of natural philosophy at the Royal Institution of Great Britain, which he resigned in 1905. From 1887 to 1896 he was Secretary to the Royal Society. From 1892 to 1901 he was Lord Lieutenant of Essex. In 1905 he became president of the Royal Society, retaining this office till 1908, in which year he was chosen to succeed the eighth Duke of Devonshire as Chancellor of Cambridge University.

Lord Rayleigh's early mathematical and physical papers, written under the name of J. W. Strutt, made him known throughout Europe.

A great part of his theoretical work has consisted in reinvestigating familiar subjects and elaborating their respective data into precision. In this way he has gone over a great portion of the field of physics, and in many cases has either brought the investigation to finality for the time being, or else started new and fruitful developments. The various branches of chemical physics, particularly capillarity and viscosity, theory of gases, flow of liquids, photography, optics, color vision, wave theory, electric and magnetic problems, electrical measurements, elasticity, sound and hydrodynamics, have especially felt his influence.

The numerous scientific memoirs in which his original work is set forth were collected under his own editorship in four large volumes, the last of which was published in 1903. His most extensive work is a book on "Theory of Sound," which, in the second edition, has become a treatise on vibrations in general.

As the outcome of a long series of delicate weighings and much experimental care in the determination of the relative density of nitrogen gas, he made, in collaboration with Sir William Ramsay, the discovery of argon.

He has taken much interest in abnormal psychological investigations, and became a member and vice-president of the Society for Psychical Research.

Lord Rayleigh was one of the original members of the Order of Merit, instituted in connection with the coronation of King Edward VII. He is a past president of the Royal Society and Nobel laureate, having been awarded a Nobel prize in 1904. He is an officer of the Legion of Honour.

# SIR WILLIAM RAMSAY, K.C.B., LL.D., D.Sc., M.D., Ph.D., F.R.S., F.C.S.

SIR WILLIAM RAMSAY was born in Glasgow on October 2, 1852. In his fourteenth year he matriculated at Glasgow University and there commenced his studies in chemistry, first under Sir William Thomson and then under Tatlock, and appears to have distinguished himself so decidedly that the latter often made him his deputy.

In 1870 Sir William continued his studies in Germany, passing one term with Bunsen and then moving to Fittig's laboratory at Tübingen. He was there inducted into the usual methods and problems of organic chemistry.

In 1872 he returned to his native city and was for two years laboratory assistant in the Young Laboratory of Chemistry, at Anderson's College. He was then appointed Tutorial Assistant of Chemistry in Glasgow University, a position which he held for six years. He there acquired a very extensive and profound knowledge of the whole field of chemistry, especially of inorganic chemistry.

In 1880 he was appointed to the chair of chemistry at University College, Bristol, and a year later he was made principal of the college. He continued at Bristol until 1887, when he was appointed to the highly-esteemed chair of chemistry at University College, London.

At this point began that rapid succession of researches which brought Sir William to scientific eminence. The measurements of surface tensions up to the critical temperature led to the well-known law which allows us to determine molecular weights in liquids. His work with Lord Rayleigh on the solution of the problem concerning the difference in density between atmospheric nitrogen and that obtained from compounds led to the discovery of argon in 1897. The periodic law immediately suggested

the existence of a number of other elements of the same type, and Sir William succeeded in a short time in discovering helium. Three further elements of the same group—neon, krypton and xenon—were afterward discovered by Sir William, associated with Morris William Travers.

As the result of an investigation taken up by him, following Becquerel's discovery of the dark rays of uranium, Sir William made his greatest discovery—that of the apparent transmutation of one element into another. The gaseous emanation of radium, which at first had behaved as an entirely new body, showed after some time the lines of helium, and, finally, it was definitely proved that radium in its spontaneous decomposition produced helium in a perfectly regular way.

Following this up, Sir William originated a series of other investigations, some of which are not yet completed, but which may be expected to result in further achievements of a high order.

Sir William is the author of numerous publications and papers. Some of the most important of these are:

"The Molecular Surface-Energy of Liquids."

"Argon, a New Constituent of the Atmosphere" (in conjunction with Lord Rayleigh).

"Helium, a Constituent of Certain Minerals."

"Neon, Krypton, and Xenon."

"The Transmutation of Radium into Helium" (with Mr. F. Soddy).

"The Discovery of the Constituents of the Air."

Three Text-books on Chemistry.

Many academic honors and various orders of distinction have been conferred upon Sir William Ramsay in recognition of his brilliant discoveries in chemistry. Among the orders are those of the Commander of the Crown of Italy; Officier de la Legion d'Honneur; Corresponding Member of the Institute of France; Hon. Member Royal Academies of Ireland, Berlin, Bohemia, Holland, Rome, St. Petersburg, etc.

Sir William is a member of numerous learned and scientific societies, among them being the German Chemical Society; American Philosophical Society, Pharmaceutical Society; Philosophical Societies of Manchester, and Rotterdam.

He was created K.C.B. in 1902, and in 1904 he was awarded the Nobel prize for his chemical researches.

## EMIL FISCHER, Ph.D., M.D., Ing.D.Sc., F.R.S.

EMIL FISCHER was born at Euskirchen, in Rhenish Prussia, on October 9, 1852. After studying chemistry at Bonn, he went to Strassburg, where he was graduated Ph.D. in 1874. He then acted as assistant to Adolph von Baeyer for eight years, after which he was appointed to the chair of

chemistry successively at Erlangen (1882) and Würzburg (1885). In 1892 he succeeded A. W. von Hoffmann as professor of chemistry at Berlin.

Dr. Fischer devoted himself entirely to organic chemistry, and in 1875, the year following his engagement with von Baeyer, he published his discovery of the organic derivatives of a new compound of hydrogen and nitrogen, which he named hydrazine. He investigated both the aromatic and aliphatic derivatives, establishing their relation to the diazo compounds, and perceiving the readiness with which they entered into combination with other substances, he originated a large number of hitherto unknown compounds; including particularly the hydrozones, which result from the interaction of the aldehydes and ketones. His observations, published in 1886, that such hydrozones, by treatment with hydrochloric acid and zinc chloride, yielded derivatives of indol, the pyrrol of the benzene series and the parent substance of indigo, were a confirmation of the views advanced by his master, von Baeyer.

His further discovery was that phenyl hydrazine reacted with the sugars to form substances which he named osazones, and which, being highly crystalline and readily formed, served to identify such carbohydrates more definitely than had been previously possible.

Turning his attention to the rosaniline dyestuffs, he published papers in 1878 to 1879 which established that these dyestuffs were derivatives of triphenyl methane.

His next research was with compounds related to uric acid. In 1881-2 he published papers establishing the formulæ of uric acid, xanthine, caffeine, etc. In 1894 he commenced the publication of that notable series of papers wherein these compounds were all referred to a common base, purin. Concurrently, he took up the investigation of the sugar group and became the recognized pioneer in this field of investigation. Dr. Fischer synthesized fructose, glucose, etc., and prepared several stereoisomerides, completing a brilliant experimental research and confirming Van't Hoff's theory of the asymmetric carbon atom. As an outcome of his study of the sugars, he attacked the problem presented by ferments and enzymes. In this connection he discovered that the chemical constitution of a sugar is related to that of the ferment and enzyme which breaks it down.

He entered on perhaps his greatest work when he commenced the study of the chemistry of the proteins. By the introduction of new methods, Dr. Fischer succeeded in breaking down the complex albuminoid substances into amino acids and other nitrogenous compounds, the constitution of most of which have been solved. By bringing about the recombination of these units appropriately chosen, he prepared synthetic peptides which approximate to the natural products.

His publications include his "Untersuchungen über Aminosäuren, Polypeptide and Proteine;" "Untersuchungen in der Purin Gruppe;" "Untersuchungen über Kohlenhydrate und Fermente."

He was awarded the Nobel Prize for chemistry in 1902.

## CHARLES PROTEUS STEINMETZ, A.M., Ph.D.

Dr. Charles Proteus Steinmetz was born April 9, 1865, at Breslau, Germany. He was educated at the Breslau Gymnasium and University, studying mathematics, astronomy, physics, chemistry, and other branches including economics. In Switzerland he studied mechanical engineering at the Polytechnicum of Zurich. In 1889 he came to America, and found a position with the Eickemeyer-Field Manufacturing Company, first as draftsman, then as electrical engineer and designer, and finally on research work in charge of the Eickemeyer Laboratory. With the absorption of the Eickemeyer interests by the General Electric Company, Dr. Steinmetz was attached to Mr. H. Parshall's calculating department in Lynn, Mass. When the company's headquarters were transferred to Schenectady, N. Y., in the spring of 1894, he organized and took charge of the calculation and design of the company's apparatus and of the research and development work. Since 1902 he has been Professor of Electrical Engineering at Union University, at the same time retaining his connection with the General Electric Company as consulting engineer, organizing and assuming charge of a Consulting Electrical Department in 1911.

In 1902 Harvard University conferred upon him the honorary degree of Master of Arts, and in the following year he was created Doctor of Philosophy by Union University.

Dr. Steinmetz is a fellow of the American Association for the Advancement of Science, a member of the Mathematical Society and of the Physical Society. He is a Past President and member of the American Institute of Electrical Engineers.

He published his "Theory and Calculation of Alternating Current Phenomena" in 1897 (fourth edition, 1908); "Theoretical Elements of Electrical Engineering," 1901 (third edition, 1909); "Theory and Calculation of Transient Electrical Phenomena and Oscillations," 1909 (second edition, 1911); "General Lectures on Electrical Engineering," 1908 (third edition, 1909); "Radiation, Light, and Illumination," 1909 (second edition, 1911); "Engineering Mathematics," 1910. These works are standard text-books in electrical engineering, as well as books of reference to the practical engineer.

He is the author of numerous papers on scientific and electrical subjects, most of which have been published in the "Transactions of the American Institute of Electrical Engineers." He read a paper on "The Physiology of Light" before the Engineers' Club of Philadelphia in 1910, and another on "Some Unexplored Fields in Electrical Engineering" before The Franklin Institute in March, 1911. He contributed an article on "Electric Transients" to the Journal of The Franklin Institute in July, 1911.

Dr. Steinmetz has done much constructive work in the electrical art, having made many important improvements in alternating current motors, generators, converters, regulators, lighting, and the like.

#### ISHAM RANDOLPH, D.Eng.

Dr. Isham Randolph was born at New Market, Clark County, Virginia, in 1848. His education, both general and technical, was acquired in the school of experience.

He entered the service of the Baltimore & Ohio Railroad in 1868,

going to the Lehigh Valley Railroad three years later.

In March, 1872, Dr. Randolph re-entered the service of the Baltimore & Ohio Railroad and later was resident engineer for a part of its western system. From 1876 to 1885, he had an extensive experience in the building of railroads, railroad terminals, and freight houses in the western section of the country.

In this latter year he opened an office for general engineering work in Chicago. In 1886 he was employed by the Illinois Central Railroad in the location and building of the Chicago, Madison & Northern Railroad and the Freeport & Dodgeville line as chief engineer. In 1888 he resumed the general practice of engineering in the city of Chicago, and was employed as engineer on various projects and later as consulting engineer for the Union Stock Yards and Transit Company and the Baltimore & Ohio Railroad Company.

On July 7, 1893, he was elected chief engineer of the Sanitary District of Chicago, and he served in this capacity for fourteen years, during the entire period of construction of the Chicago Sanitary and Ship Canal, a project costing some sixty millions of dollars. He retired as chief engineer in 1907, and has since served the Sanitary District as consulting engineer.

He was appointed by President Roosevelt on the Board of Consulting Engineers for the Panama Canal, and was one of the five members of the board whose minority report was accepted by the President and Secretary of War, approved by the Panama Commission, adopted by Congress, and the canal is now being constructed in accordance with its recommendations.

In 1908 President Roosevelt invited him to be one of the six engineers whom he wished to have accompany President-elect Taft to Panama to consider "whether or not there is any reason to change the plans upon which we are working." This Board of Engineers submitted its report to the President on Tuesday, February 16, 1909, unanimously upholding the plans for the lock canal across the Isthmus.

Dr. Randolph recently served the city of Milwaukee as consulting engineer on its harbor project and prepared comprehensive plans for harbor improvement there.

He was chairman of the Internal Improvement Commission of Illinois, which commission was charged with the duty of planning the deep waterway from Lockport to Utica, for which the State voted an issue of \$20,000,000 in bonds. He is a member of the Illinois State Conservation Commission. He is a member of the Harbor Commission of the city of Chicago, and is consulting engineer for important engineering projects in Toronto, Canada, Buffalo, N. Y., and Baltimore, Md., besides other minor projects in various localities. He is a member of the Rivers and Lakes Commission of the State of Illinois.

In 1910 the University of Illinois conferred upon him the degree of Doctor of Engineering.

He is a past president of the Western Society of Engineers and a member of the American Society of Civil Engineers.

#### EMILE BERLINER.

EMILE BERLINER was born in Hanover, Germany, May 20, 1851. He was educated in the public schools of that city, and in the Samson High School, Wolffenbüttel, graduating from the latter in 1865. Five years later he came to America and, while engaged in a mercantile pursuit, took up the study of the electric transmission of speech. In 1877 he invented the loose-contact telephone transmitter bearing his name, and which brought Bell's great invention of the preceding year within the range of commercial application and practical use. In the same year he effected another great advance in the telephone art by an application of the induction coil to step-up the low-tension variable current through the loose-contact transmitter to a higher tension variable current capable of better overcoming the impedance of long lines. This loose contact has made the telephone the instrument that it is to-day.

In 1878, on the formation of The Bell Telephone Company, Mr. Berliner accepted the position of Chief Inspector of Instruments at its works in Boston, and in that capacity the first twenty thousand transmitters that went into use passed through his hands.

In 1881 Mr. Berliner, retaining his connection with The Bell Telephone Company, as consulting expert, removed to Washington, and besides bringing out a number of other inventions relating to telephony, devoted his attention to the improvement of the talking machine. In 1887 he invented the gramophone, the first talking machine which utilized a record having a groove of even depth and varying direction and in which the record groove not only vibrates the recording stylus but also propels it. This invention was exhibited by Mr. Berliner before The Franklin Institute in 1888 and was subsequently awarded a John Scott Medal by the City of Philadelphia, on the recommendation of the Institute.

The Berliner Gramophone, now known in America as the "Victor" Talking Machine, and throughout the world under various other trade names, has become the basis of a great and growing industry and an important agency of education and culture. Its popularization has been largely due to the system invented by Mr. Berliner for accurately and cheaply duplicating the original records.

Mr. Berliner has latterly extended his inventive efforts into the field of aviation and has given much attention to the possibilities of the Helicopter as a means of artificial flight. In this field he has also made notable progress toward perfecting a multicylinder motor of the internal combustion type, and has succeeded in greatly reducing its weight in proportion to its power. His engine of this type produced in 1907-8, with a capacity of 35 horsepower, weighed but 97 pounds. These were the first revolving

cylinder motors successfully applied in aëronautical work and led the way to the extensive adoption of this type of motors for aëroplanes in Europe.

In addition to his activity as an inventor Mr. Berliner has given largely of his time to the study of the pathology of milk. His campaign of education on this subject led to the Washington Milk Conference of 1907, and his efforts have been fruitful of beneficial results. In this department of hygiene, as well as in his immediate field of research and invention, Mr. Berliner has made numerous contributions to scientific and technical literature.

# LETTERS RECEIVED FROM ELLIOTT CRESSON MEDAL RECIPIENTS WHO WERE NOT PRESENT AT THE STATED MEETING IN MAY.

APRIL 25, 1913.

4, Carlton Gardens, Pall Mall, S. W.

DEAR SIR:

I have to-day received the Elliott Cresson Medal with its highly flattering inscription.

I beg you to communicate to the Institute my high appreciation of this compliment.

I am, respectfully,

RAYLEIGH.

Dr. R. B. Owens,
Franklin Institute,
Philadelphia, U. S. A.

19 CHESTER TERRACE, REGENT'S PARK, N. W., 28th April, 1913.

MY DEAR SIR:

I received an official and also a personal letter from Mr. Bryce, saying that he had been commissioned to transmit to me the Elliott Cresson Medal, and two days later I received the medal and the diploma.

It is with feelings of much gratification that I receive this medal; to be associated with such distinguished recipients is a great honour; and to find that my work receives recognition from such a well-known body as The Franklin Institute conveys much pleasure.

May I ask you to be so good as to transmit to the members of the Institute and to those of the Committee on Science and Arts my warm thanks for the honour which they have conferred on me.

I am, dear sir, yours very truly,

WILLIAM RAMSAY.

WALTON CLARK, ESQ.,
THE FRANKLIN INSTITUTE,
PHILADELPHIA.

BERLIN N., den 10 Mai, 1913. Hessische Strasse 2.

To Mr. R. B. OWENS,

Secretary of the Franklin-Institut,

Philadelphia.

Hochverehrter Herr:

Ich habe die Ehre, Ihnen mitzuteilen, dass ich gestern durch Vermittlung unserer Regierung die goldene Elliott Cresson Medal erhielt, die das Franklin-Institut mir verliehen hat.

Aus dem beigefügten Diplom und Ihrem werten Brief vom 2 April d. J. ersehe ich, dass die Verleihung auf Vorschlag des Committee on Science and the Arts geschehen ist.

Die Anerkennung meiner wissenschaftlichen Bestrebungen durch Ihr angesehenes Institut, welches den Namen eines der grössten Naturforscher und Staatsmänner trägt, betrachte ich als eine ganz besondere Auszeichnung, and ich bitte Sie, meinen warmen Dank dafür dem Herrn Präsidenten and dem wissenschaftlichen Komitee, das mich vorgeschlagen hat, übermitteln zu wollen.

Mit vorzüglicher Hochachtung, Ihr ergebener,

EMIL FISCHER.

#### COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the June Stated Meeting.)

HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, June 4, 1913.

MR. J. A. P. CRISFIELD in the Chair.

The following report was presented for final action:

No. 2526.—C. Francis Jenkins's Motion Picture Apparatus. Scott Award recommended. Adopted.

The following were recommended for examination and accepted:

No. 2542.—Batdorf Coin-Handling System.

No. 2543.—The Draeger Oxygen Company's Pulmotor.

No. 2544.—Kinkead Shaft-Leveling Machine.

Other business included adoption of report of Subcommittee on Literature for 1912.

R. B. Owens, Secretary.

#### MEMBERSHIP NOTES.

#### Elections to Membership.

(Stated Meeting of the Board of Managers, June 11, 1913.)

#### RESIDENT.

Mr. Lewis Audenried, Eddystone, Pa.

MR. O. B. EVANS, The United Gas Improvement Company, Broad and Arch Streets, Philadelphia, Pa.

PROF. R. H. FERNALD, University of Pennsylvania, Philadelphia, Pa.

Mr. A. E. Gibbs, Pennsylvania Salt Manufacturing Company, Greenwich Point, Philadelphia, Pa.

MR. H. K. HATHAWAY, 7215 Cresheim Road, Mt. Airy, Philadelphia, Pa.

Mr. M. G. Kennedy, The United Gas Improvement Company, Northwest Corner Broad and Arch Streets, Philadelphia, Pa.

MR. WM. H. McMurray, 1502 Master Street, Philadelphia, Pa.

MR. SIDNEY MASON, President, Welsbach Company, Broad and Arch Streets, Philadelphia, Pa.

Mr. Robert Radford, Secretary, Standard Steel Works Company, Morris Building, Philadelphia, Pa.

MR. H. V. WILLE, The Baldwin Locomotive Works, Philadelphia, Pa.

#### NON-RESIDENT.

Dr. H. V. Arny, Columbia University, College of Pharmacy, 115 West Sixty-eighth Street, New York City.

Mr. Edwin S. Barnett, Mt. Alverno, Delaware County, Pa.

MR. S. LAWRENCE BIGELOW, 1520 Hill Street, Ann Arbor, Mich. MR. CLAYTON O. BILLOW, 416 West Indiana Street, Chicago, Ill.

MR. RANDOLPH BOLLING, U. S. Navy Yard, Norfolk, Va.

Prof. F. W. Bushong, University of Kansas, Lawrence, Kans.

MR. HERBERT H. Dow, The Dow Chemical Company, Midland, Mich.

Mr. IRENEE DU PONT, Wilmington, Del.

MR. JOHN CALDER, First Vice-President, International Motor Company, Broadway and Fifty-seventh Street, New York, N. Y.

Dr. Frank K. Cameron, Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

MR. HAROLD V. COES, First National Bank Building, Boston, Mass.

Mr. W. A. Converse, Secretary, Dearborn Chemical Company, McCormick Building, Chicago, Ill.

Mr. Charles Engelhard, Hudson Terminal Building, 30 Church Street, New York, N. Y.

Mr. Persifor Frazer, Jr., Vice-President, Harlan & Hollingsworth Corporation, Wilmington, Del.

MR. FREDERICK A. GEIER, President, The Cincinnati Milling Machine Company, Cincinnati, Ohio.

Mr. N. J. Gould, President, The Goulds Manufacturing Company, Seneca Falls, N. Y.

Dr. Edward Gudeman, 903-4 Postal Telegraph Building, Chicago, Ill.

Mr. James Hartness, President, Jones & Lamson Machine Company, Springfield, Vt.

Mr. Ellwood Hendrick, 30 Pine Street, New York, N. Y.

Prof. Chas. H. Herty, University of North Carolina, Department of Chemistry, Chapel Hill, N. C.

MR. JOHN W. HORNSEY, 233 Broadway, New York, N. Y.

Prof. J. H. James, Carnegie Institute of Technology, Department of Chemical Engineering, Schenley Park, Pittsburgh, Pa.

MR. F. HEDLEY JOBBINS, Aurora, Ill.

Mr. A. KLIPSTEIN, 644-654 Greenwich Street, New York, N. Y.

Mr. H. J. Krebs, President, The Krebs Pigment and Chemical Company, Newport, Del.

Prof. V. Lenher, The University of Wisconsin, Department of Chemistry, Madison, Wis.

PROF. CHARLES E. LUCKE, 117th Street and Broadway, New York, N. Y.

MR. NELSON B. MAYER, 27 William Street, New York, N. Y.

MR. EUGENE MERZ, Box 216, Newark, N. J.

MR. HERMAN A. METZ, 122 Hudson Street, New York, N. Y.

Mr. Fred. J. Miller, 293 Broadway, New York, N. Y.

Prof. Edmond O'Neill, University of California, College of Chemistry, Berkeley, Cal.

Prof. S. W. Parr, University of Illinois, Urbana, Ill.

Dr. ISHAM RANDOLPH, 826 First National Bank Building, Chicago, Ill.

MR. WALTER RAUTENSTRAUCH, 117th Street and Broadway, New York, N. Y.

Mr. Franz Roessler, Perth Amboy, N. J.

Dr. Allen Rogers, Pratt Institute, Brooklyn, N. Y.

Mr. G. N. Sægmuller, 1100 St. Paul Street, Rochester, N. Y.

MR. H. J. SKINNER, Arthur D. Little, Inc., 93 Broad Street, Boston, Mass. Prof. Alexander Smith, Columbia University, Department of Chemistry, New York, N. Y.

MR. A. B. STITZER, 3744 North Carlisle Street, Philadelphia, Pa.

Mr. I. F. Stone, National Aniline and Chemical Company, 100 William Street, New York, N. Y.

Mr. Orin C. Stout, Ellwood City, Pa.

Prof. H. P. Talbot, Massachusetts Institute of Technology, Department of Chemistry and Chemical Engineering, Boston, Mass.

Dr. John E. Teeple, 50 East Forty-first Street, New York, N. Y.

MR. JOHN L. TUFTS, P. O. Box 22, Winchester, Mass.

Mr. Herbert A. Wagner, Vice-President, Consolidated Gas, Electric Light and Power Company, Lexington and Liberty Streets, Baltimore, Md.

## Changes of Address.

MR. JOHN W. BRASSINGTON, 902 Van Buren Street, Wilmington, Del. REAR-ADMIRAL JOSEPH B. MURDOCK, U. S. N., Danbury, N. H. MR. J. STEPH. VAN DER LINGEN, Stapfer Strasse 23, Zurich, Switzerland.

# NECROLOGY.

Adolphus Bonzano was born in 1830 at Ehingen, Germany, and was educated in the gymnasia of Ehingen, Dinsdorf, and Stuttgart. While he was yet a boy his father emigrated to Texas.

Mr. Bonzano came to Philadelphia in 1850, and after two years went to Springfield, Mass., where he entered the Reynolds Machine Works, becoming superintendent at the completion of his apprenticeship. He was employed in the mechanical departments of various machine works and railroad shops for a few years, and in 1865 had charge of the construction of the Detroit Bridge and Iron Works. In 1868 he went to Phœnixville and, with the late Thomas C. Clarke and others, organized the Phœnix Bridge Company, of which he was president and chief engineer until 1893. During the next five years he was associated with Mr. Clarke in New York as a consulting engineer, after which he devoted his energies to his inventions of railroad and other engineering appliances.

Mr. Bonzano was elected to membership of the Institute in 1900.

John W. Ridpath was born in Upper Onslow, Novia Scotia, in 1840. At an early age he removed to Pittsburgh, Pa., and later to Jenkintown, Pa., where he resided until his death, on May 8th.

He was for several years engaged in business pursuits, becoming a druggist in 1870. Since 1885 he had served in several local public offices, and was for five years a Justice of the Peace. He was also connected with several turnpike road companies, and was superintendent of the local turnpikes under the Philadelphia Rapid Transit Company.

Mr. Ridpath was a noted local historian, and many of his articles appeared in various magazines. He was also much interested in photography and microscopy.

He was connected with the following societies: Jenkinstown Lyceum Association, Abington Library Society, American Good Roads Association, Bucks County Historical Society, National Geographical Society, The Philadelphia College of Pharmacy, The Pennsylvania Pharmaceutical Association, and many fraternal and secret organizations.

His membership in the Institute began in 1881; he took an active interest in its work, both by lecturing on several occasions before its Photographic Section and also as a member of its Committee on Science and the Arts since 1891.

#### LIBRARY NOTES.

#### Purchases.

ABNEY, W. DE W.— Researches in Colour Vision. 1913.

BOGÆRT, ED. W.—L'Effet gyrostatique et ses applications. 1912.

CANTELL, M. T.—Reinforced Concrete Construction. 1912.

CHRISTIE, W. W.—Water: its purification and use in the industries. 1912.

CODD, M. A.—Electrical Ignition for Internal Combustion Engines. 1911.

FISCHER, A.—Elektroanalytische Schnellmethoden. 1908.

Frodiar Iron and Steel Company Publication.—Handbook for Iron Founders.

GRUENWALD, J.—The Technology of Iron Enamelling and Tinning. 1912.

HERRMANN, G.—The Graphical Statics of Mechanism. 1904.

HURST, H. E. and R. T. LATTEY.—A Text-book of Physics. 3 volumes. 1912. LE MAITRE, W.—Natural Stability and the Parachute Principle in Aëroplanes. 1911.

Levy, D. M.-Modern Copper Smelting. 1912.

LUNGE, G.—The Manufacture of Sulphuric Acid and Alkali. Vol. 1. 4th edition. 3 volumes. 1913.

MACLAURIN, R. C.—The Theory of Light. Part 1. 1908.

MASTIN, JOHN.—The Chemistry, Properties, and Test of Precious Stones.

RAPER, C. L.—Railway Transportation. 1912.

RICHARDSON, C.—Asphalt Construction for Pavements and Highways. 1913. Royal Society of Edinburgh.—Transactions. Vol. 49, pt. 1. 1912.

Royal Society of London.—Catalogue of Scientific Papers 1800 to 1900. Vols. 2 and 3, pt. 1. 1909 and 1912.

THOMPSON, N. S.—Mechanical Equipment of Federal Buildings. 1912.

Thomson, J.—Collected Papers in Physics and Engineering. 1912.

WILLCOCKS, W.—The Irrigation of Mesopotamia. 2 volumes. 1911.

Wilson, H. A.—The Electrical Properties of Flames. 1912.

Wood, F.-Modern Road Construction. 1912.

Wood, J. T.—The Puering, Bating, and Drenching of Skins. 1912.

ZSIGMONDY, R.—Colloids and the Ultra-Microscope. 1909.

#### Gifts.

L'Academie Royale de Belgique, Annuaire, 1913. Brussels, 1913. (From the Academy.)

American Fertilizer Hand Book, 1913. Philadelphia, 1913. (From Ware Brothers Company.)

American Institute of Mining Engineers, Transactions, vol. 43. New York, N. Y., 1913. (From the Institute.)

American Pharmaceutical Association, Proceedings, vol. 59, 1911. Scio, Ohio, 1912. (From the Association.)

Bangor Public Library, Annual Report, 1912. Bangor, Maine, 1913. (From the Library.)

Chicago School of Civics and Philanthropy, Alumni Register 1903-1913. Chicago, 1913. (From the School.)

College of William and Mary, Catalogue 112-1913. Williamsburg, Va., no date. (From the College.)

Concord Water Department, 41st Annual Report, 1912. Concord, N. H., 1913. (From the Department.)

Connecticut State Board of Health, 32d Report, 1911-1912. Hartford, 1913. (From Secretary of the Board.)

Finland Arbetesstatistik, xv. Undersökning angænde Glasindustrin. Helsingfors, Finland, 1913. (From the Finland Patent Office.)

Geological Survey of New Jersey, Bulletin No. 8, Annual Administrative Report of the State Geologist for 1912. Trenton, 1913. (From the Survey.)

Huther Brothers Saw Manufacturing Company, Catalogue No. 33. Rochester, N. Y., 1913. (From the Company.)

Illinois Bureau of Labor Statistics, 14th Annual Report. Springfield, 1913. (From the Bureau.)

John Crerar Library, 18th Annual Report, 1912. Chicago, 1913. (From the Library.)

Kansas State Board of Agriculture, 18th Biennial Report, 1911 and 1912. Topeka, 1913. (From the Board.)

Leland Stanford Junior University, Register 1912-13. Stanford University, Cal., 1913. (From the University.)

Liverpool Engineering Society, Transactions, vol. 33. Liverpool, 1912. (From the Society.)

Louisiana State Museum, Third Biennial Report of the Board of Curators. New Orleans, 1912. (From the Museum.)

Madison Board of Water Commissioners, 30th Annual Report. Madison, Wis., 1913. (From the Board.)

National Academy of Sciences, Memoirs, vol. 11. Washington, D. C., 1913. (From the Academy.)

Nevada Railroad Commission, 5th Annual Report, 1912. Carson City, 1913. (From the Commission.)

New Jersey Geological Survey, Bulletin No. 9a, Preliminary Report of the Archæological Survey of the State of New Jersey. Trenton, N. J., 1913. (From the Survey.)

New York State Public Service Commission for the First District, Report 1911, vol. 2. New York, N. Y., no date. (From the Commission.)

Ontario Department of Agriculture, Annual Report 1911, vols. 1 and 2. Toronto, Can., 1913. (From the Department.)

Ontario Department of Agriculture, Report of the Women's Institutes, 1913, part 2. Toronto, Can., 1913. (From the Department.)

Philadelphia Board of City Trusts, 43d Annual Report of the Directors, 1912. Philadelphia, 1913. (From the Board.)

Philadelphia Free Library, 17th Annual Report, 1912. Philadelphia, 1913. (From the Library.)

Providence Public Library, 35th Annual Report, 1912. Providence, R. I., 1913. (From the Library.)

Rainfall Data of India for 1911. Calcutta, 1912. (From the Meteorological Office.)

Rensselær Polytechnic Institute, Catalogue March, 1912. Troy, N. Y., 1912. (From the Institute.)

Republica Argentina Anales de la Biblioteca, Tomo 8, 1912. Buenos Aires, 1912. (From Comision Protectoria de Bibliotecas Populares.)

Rhode Island State Public Utilities Commission, Annual Report 1912. Providence, 1913. (From the Commission.)

- Société de Physique de Geneve, Compte Rendu des Seances 29, 1912. Geneve. Switzerland, 1913. (From the Society.)
- Société Internationale des Électriciens, Annuaire 1913. Paris, 1913. (From the Society.)
- Society of Naval Architects and Marine Engineers, Transactions, vol. 20, 1912. New York, no date. (From the Society.)
- The 1900 Solar Eclipse Expedition of the Astrophysical Observatory of the Smithsonian Institution, by S. P. Langley. Washington, D. C., 1904. (From the Smithsonian Institution.)
- Temple University, Annual Catalogue 1913-14. Philadelphia, 1913. (From the University.)
- United States Department of Commerce, Commerce and Navigation, 1912. Washington, D. C., 1912. (From the Department.)
- United States Department of Commerce, Statistical Abstract of the United States, 1912. Washington, D. C., 1913. (From the Department.)
- United States Interstate Commerce Commission, 26th Annual Report, 1912. Washington, D. C., 1913. (From the Commission.)
- University of Minnesota, Studies in Economics, No. 1. Minneapolis, 1913. (From the University of Minnesota Library.)
- University of Nebraska, 43d Annual General Catalog. Lincoln, 1913. (From the University.)
- University of Pittsburgh, Catalog 1912-13. Pittsburgh, 1913. (From the University.)
- University of Tennessee, Register 1912-13. Knoxville, 1913. (From the University.)
- Ursinus College, Catalogue 1912-13. Collegeville, Pa., no date. (From the College.)
- Vermont School Report for 1912 and State Geologist Report for 1911-12.

  Montpelier, 1912. (From the State Librarian.)
- Western Australian Institution of Engineers, Proceedings, vol. 3, No. 1. November, 1912. Perth, 1912. (From the Institution.)
- Western Society of Engineers, Year Book 1913. Chicago, 1913. (From the Society.)
- Wisconsin State Historical Society, Proceedings 1912. Madison, 1913. (From the Society.)

#### BOOK NOTICES.

- THE EXAMINATION OF WATERS AND WATER SUPPLIES. John C. Thresh, D. Sc., 2d edition, 8vo., 624 pages and index, illustrated, Philadelphia, P. Blakiston's Son & Co. \$5.
- Dr. Thresh is so well known in this field that we can be sure that the work before us will be comprehensive and valuable. The subject-matter is divided into three parts: Examination of the sources of water, interpretation of analytic methods and analytic processes. Many interesting examples are detailed of the problems confronting the sanitary engineer in dealing with the increased demand and increased pollution of water in highly-civilized com-

munities. In connection with the microscopic examination of water sediments, many of the common vegetable and animal forms encountered in such work are figured, the degree of magnification being generally given. This is an important point, that should never be neglected in representing microscopic fields.

Notwithstanding Dr. Thresh's familiarity with the literature of the subject, and, as noted by a remark in the book, actual observation of the work in American laboratories, his own point of view is almost exclusively English, and in some respects quite old-fashioned, although it is not intended by this term to indicate that the methods are not trustworthy. Still, the reviewer cannot see any excuse for such a term as "permanganate of potash," which occurs several times in the volume. Nor does there appear to be any scientific consistency in the spellings "grammes" and "milligrams."

In the determination of nitrates, Dr. Thresh uses the copper-zinc couple, and specially condemns the phenolsulphonic acid method. In view of the large amount of investigation recently given to this method, especially by American chemists, it is to be regretted that the author did not give in some detail the routine he followed. From the formula he gives for preparing the reagent, it seems evident that he has not made any comparison between the copper-zinc couple method and that with phenoldisulphonic acid, which is the reagent now used largely by American chemists. It is now known that the mixture of sulphonic acids obtained in the original process of preparing the reagent is not satisfactory, and it is not likely that any careful worker uses this form. Gill took up the matter a number of years ago, and made an important step forward in suggesting the heating of the reagent for six hours in boiling water. A few years ago, Messrs. Chamot, Pratt and Redfield still more extensively investigated the method and gave an improved formula for the preparation of the reagent (J. Amer. Chem. Soc., 1911, 366). It seems to the reviewer that before a simple and rapid process is condemned it should be tried out in its most improved form.

The time is, probably, rapidly passing when either chemical or bacteriologic tests of isolated samples of surface and ordinary subsoil water will be required. The practical issues are now largely questions of engineering, and, so far as surface water is concerned, it has long been known that in an unfiltered condition it is always unsafe for general use, and we need no specific biologic or abiologic datum to tell us this.

HENRY LEFFMANN.

GENERAL INDEX TO THE CHEMICAL NEWS, Vols. 1 to 100. Chemical News Office, London. 712 pages, 26 x 18 cm. Price, \$10.

This index covers the first one hundred volumes of the journal in question in what appears to be a very thorough way. Each page contains three columns of small but clear type. The articles are listed both under author and subject, but the two departments are not separated. The index seems very complete and forms an interesting survey of the period covered by it. It should be of great value to chemists who possess files of the *Chemical News*.

ROBERT H. BRADBURY.

THE INDUSTRIAL ARTS INDEX. A cumulative index to engineering and trade periodicals. Published by the H. W. Wilson Company, Minneapolis, Minn.

The first issue of this publication, dated February, 1913, contains a list of the articles which appeared in January and February in forty-three leading periodicals in the English language devoted to the various branches of engineering, chemistry, mining and metallurgy, and other industrial fields.

The second number indexes, in one alphabet, all articles published during

the four months, January to April, in nearly fifty magazines.

The index is arranged on the dictionary plan and contains in addition to the author entry as many subject entries as the contents demand. Cross references point the way to material on allied subjects. Volume number, page, and date are given for each article, and note is also made when illustrations accompany it.

The index will appear five times in each year, each number will be fully cumulated to date of issue, and the December issue will be the annual cumulation. It is the intention to increase the number of magazines to be indexed from time to time, and by the end of the current year the number will reach

80, increasing ultimately to about one hundred.

No flat subscription rate has been made; instead, a sliding scale of prices will apply, the rate to each subscriber is to be determined by the number of periodicals subscribed for which are indexed. Further details may be had from the publishers.

#### PUBLICATIONS RECEIVED.

Chronique Illustrée du Concours International de Telegraphie Pratique. Souvenir des événements professionels qui eurent lieu à Turin, Rome, Milan et Côme en 1911 et au succès desquels tout le monde a si bien contribué. Fernando Geronimi, 184 + 151 pages, illustrations, foliò. Milano, chez l'Auteur, no date.

Philippine Islands Bureau of Science, Eleventh Annual Report of the Bureau to the Honorable the Secretary of the Interior, by Alvin J. Cox, Acting Director of the Bureau of Science, for the year ending August 1, 1912. 83 pages, illustrations, plates, 8vo. Manila, Bureau of Printing, 1913.

Canada Department of Mines, Mines Branch: Annual Report on the Mineral Production of Canada during the Calendar Year 1911 John McLeish, B. A., Chief of the Division of Mineral Resources and Statistics. 316 pages, 8vo. Ottawa, Government Printing Bureau, 1913.

Canada Department of Mines, Mines Branch: The magnetic Iron Sands of Natashkwan, County of Saguenay, Province of Quebec, by George C. Mackenzie, B. Sc. 57 pages, illustrations, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1912.

Preussische Seilfahrts-Kommission: Die Verhandlungen und Untersuchungen. II Heft. Bericht der nach England entsandten Mitglieder; Bericht der nach dem Königreich Sachsen und nach Osterreich entsandten Mitglieder; Bericht der nach Belgien und Nordfrankreich entsandten Mitglieder, bearbeitet von Professor Fr. Herbst. 60 pages, illustrations, plates, quarto. Berlin, Wilhelm Ernst & Sohn, 1913.

North Carolina Geological and Economic Survey, Joseph Hyde Pratt, State Geologist. Biennial Report of the State Geologist, 1911–12. 118 pages, 8vo. Raleigh, State Printers, 1913.

School of Mines and Metallurgy, University of Missouri, Bulletin, March, 1913. Catalogue 1912-13. 137 pages, plate, 8vo. Rolla, Mo., 1913.

Vice Commission of Philadelphia, a Report on Existing Conditions, with Recommendations to the Honorable Rudolph Blankenburg, Mayor of Philadelphia. 164 pages, 8vo. Philadelphia, published by the Commission, 1913.

Alaska Mine Inspector, First Annual Report for the Fiscal Year Ended June 30, 1912. 24 pages, tables, 8vo. Washington, Government Printing

Office, 1913.

U. S. Bureau of Mines: Technical Paper 14, Apparatus for Gas-Analysis Laboratories at Coal Mines, by George A. Burrell and Frank M. Seibert. 24 pages, illustrations, 8vo. Rules and Regulations to Govern the Coal Mines at Gebo, Wyo., leased to the Owl Creek Coal Company. 13 pages, 8vo. Monthly Statement of Coal-Mine Accidents in the United States, January, February, and March, 1913. Compiled by Albert H. Fay. 11 pages, 8vo. Washington, Government Printing Office, 1913.

Utilization of Peat. F. M. PERKIN. (Chem. Trade Journ., lii, 89.)—This article considers the utilization of peat as a high-grade fuel under certain conditions; as a source of charcoal, with the formation of gas of high calorific value, and ammonia and tar as by-products; and further as a source of power gas.

The Oil Situation in Northern Alberta.  $W_M$ . Fisher. (Petroleum Rev., xxvii, 323.)—Inconceivably large quantities of gas have been discovered. One well has been burning with terrific force for 15 years. The gas pressure is 795 pounds per square inch, and the flow is 68,000,000 cubic feet per 24 hours. Enormous deposits of tar sands have been found.

The First Attempt at the Synthesis of Nitric Acid. C. Matignon. (Rev. Scientifique, No. 12, 360.)—Madame Louise J. P. B. Lefebvre, of Paris, took out an English patent, dated April 26, 1859, under the title "Improvements in the manufacture of nitric acid and its application to the production of artificial nitrates and nitrites." Briefly, one flask is inverted over another flask. In the upper flask two poles of a battery are fixed from which an electric spark is flashed, which decomposes the air in the flask. Air is passed in a continuous current. The nitrogen oxides formed are absorbed by water or an alkaline solution in the lower flask; this water is decomposed by the electric current and so furnishes oxygen to combine with the atmospheric nitrogen.

# CURRENT TOPICS.

Fixation of Units by Legislation. R. DE BAILLEHACHE. (Rev. Gén. des Sciences, Jan. 15, 1913.)—The French Minister of Commerce and Industry has asked the various commercial, industrial, and scientific communities whether this would not be an opportune time to fix by legislation new units, such as the units of force, heat, light, and electricity, and the author reviews the whole question, mainly from the national standpoint and in anticipation of forthcoming legislation. In addition to the usual units of length, mass, etc., the term cop is proposed for the absolute unit of force on the decimal metric system. Unit of force.—The cop (an abbreviation of Copernicus) is that force which, acting on a mass of one kilogramme, gives it an acceleration of one metre per second. In published works the additional unit of force, the hectogramme, could be used. A force of one hectogramme = 0.980665 cop. Conversely, one cop = 1.01972 hectogramme (mass). Unit of work.—While the absolute unit of work or energy is the joule, in transactions the additional unit, the hectogramme-metre could be used (one hectogramme-metre = 0.980665 joule). Unit of power. —The absolute unit is the watt: this is the power generated by the displacement of a force of one cop at a speed of one metre per second. As additional unit the poncelet could be used (one poncelet = one kilowatt approximately, or exactly 0.980665 kilowatt, and is 4/3 of the older cheval-vapeur of 75 kilogrammemetres). Unit of pressure.—The absolute unit is the decabarye [decabar] (or tor, an abbreviation of Torricelli), and is the pressure exerted by the force of one cop uniformly distributed on a surface of one metre-square. The sub-multiple,  $^{1}/_{10}$ , of this is called the barye (= the pressure of a column of mercury of 750.05 millimetres in height at o° C.). In industrial work the "atmosphere" to be retained (one atmo = the weight of a column of mercury 735.5 millimetres in height at  $0^{\circ}$  C. = 98066.5 decabaryes). The normal standard atmospheric pressure = 101321.1 decabaryes, or about 1,000,000 baryes. Then follows a discussion of the definitions of the various units, and concludes with the hope that future legislation will recognize the beauty and harmony of the M. K. S. (metre, kilogramme, second) system.

Effect of Temperature and Vibration on Drawn Tungsten Filaments. O. Scarpa. (Atti dell' Assoc. Elettr. Ital., xvi, 638.)
—Drawn tungsten filaments are found to have an entirely different structure from those prepared by reduction of the oxide, the former

being fibrous, while the latter are granular. Examination of the filaments after burning in lamps for 500 hours with either a continuous current, producing a temperature of about 1900° C., or an alternating current of 42 cycles, shows that in both cases the metal is transformed into the micro-crystalline condition, just as has been previously shown to occur with the old filaments produced from the oxide. Drawn tungsten filaments should, therefore, be much more durable than drawn tantalum filaments, which form larger crystals under the combined action of temperature and vibration.

Explosion of Hydrogen Cylinders. Lelarge. Rendus, clv, 914.)—Two men were killed in 1911 while measuring the gas pressure of hydrogen in a steel cylinder. Apparently the explosion was due to the rapid compression of the air in the tube connecting the cylinder to the gauge. In experiments conducted in the Laboratoire d'Aeronautique Militaire the cylinders were placed inside a strong steel cage built up of hoops and tie-rods, and a pipe packed with disks was interposed between the cylinder and the gauge to take up any heat generated by a minor gas combustion within the gauge. The gas pressure was first determined with the safety tube in position; the gas was then analyzed, and the pressure re-determined without the safety device; explosion occurred when the hydrogen was sufficiently impure. In practice all cul-de-sac connections should be avoided or be arranged like a safety tube, and the density of the gas should be measured before taking the pressure. Great care is needed in dealing with heavy hydrogen, probably containing air or oxygen, especially if electrolytic.

Titanic Acid in Underglaze Colors. A. BERGE. xlvi, 206.)—The color produced by a stain depends, to some extent, on the reaction of the other constituents on the chief coloring oxide. Cobalt, for example, gives a deep dark-blue with silica and a sky-blue with alumina. The tints are further affected by zinc oxide, phosphoric acid, etc. The component oxides of a stain may be intimately mixed by fine grinding, by precipitation of the hydroxides, by melting together of sulphates in their water of crystallization, or by Pukall's "suction" method, in which soluble salts of coloring oxides are absorbed by kaolin, etc., and then calcined and ground. Titanic acid is recommended as a carrier for other coloring oxides. Trials were fired in majolica, stoneware, and porcelain kilns, of rutile thus used with the oxides of uranium, cobalt, iron, nickel, copper, manganese, chromium, molybdenum and tungsten. A wide range of colors was obtained from yellow to blue-black. The best results for underglaze, when using titanic acid alone, were obtained at cone 7-9 for olive-green, brown, and vellow tints.

Edeleanu's Process of Refining Petroleum Oil. C. ENGLER and L. Ubbelohde. (Z. Angew. Chem., xxvi, 177.)—This method was tested both in the laboratory and on the industrial scale. In the industrial tests the petroleum distillate to be refined was first dried by a fused mass of one part of calcium chloride and four parts sodium chloride, then pumped into a cooling chamber, some of its heat being abstracted by passing through pipes in contact with previously chilled refined oil. The liquid sulphur dioxide was chilled in a similar manner and conveyed to another cooling chamber. When both oil and reagent were cooled to about —10° C., the oil was run into a mixing chamber and the requisite quantity of liquid sulphur dioxide (1.3:1) forced to flow in a state of fine division over its surface. In this way the oil became saturated with sulphur dioxide without the need of mechanical agitation. The lower layer consisting of sulphur dioxide extract was drawn off for evaporation, while the upper refined part was drawn to another chamber. The sulphur dioxide was evaporated from both parts by steam coils, and was condensed again and returned to the liquefied gas reservoir. The refined oil then only contained about 0.2 per cent., and the extract about 0.4 per cent., of sulphur, dioxide, and this could be easily washed out with water. A plant for treating 62 tons of oil per day could easily be run by three men, and the total cost of refining 100 kilos of petroleum oil amounted to M.o.436 (5 cents per 100 pounds). The refined oil thus obtained invariably had a lower specific gravity than the original distillate, that of the extract being correspondingly higher. The refined portion from crude distillates of every kind was nearly colorless, any faint yellow color being readily removed by a slight refining with 0.5 per cent. of sulphuric acid. This refined oil burned with a strong white flame without smoke, and in these respects was equal to the best lamp oil. The extract, on the other hand, was yellow to brown in color and could not be burned in lamps. Photometric tests also showed that the lamp oil refined by the new process was superior to that refined by the ordinary method, and that it was nearly equal in intensity of light to the best American oils. The extract consisted chiefly of unsaturated hydrocarbons, homologous compounds to benzene, etc., and could be used in the preparation of substitutes for oil of turpentine, and especially for such purposes as oils rich in unsaturated hydrocarbons (e.g., oils from Borneo and Texas) are used. In fact, these extracts would be more suitable than the natural oils mentioned, as solvents for many resins. The constituents boiling above 200° C. could not be used for this purpose, but might be used as lubricants and gas oils, while the tar obtained in the latter process would contain a considerable quantity of the lower aromatic hydrocarbons, which would increase its value under certain conditions.

 $\beta$ -Gold. M. Hanriot and F. Raoult. (Bull. Soc. Chim., xiii, 260.)—Finely-divided annealed gold is found to be appreciably attacked by boiling nitric acid; 0.076 gramme of metal is dissolved from 5 grammes of gold by 100 c.c. of monohydrated acid in two hours; and brown gold is still more soluble, 1.54 grammes being dissolved under the same conditions. Brown gold is dissolved more readily than yellow gold by a solution of auric chloride in the presence of hydrochloric acid, giving a solution which on cooling yields a crystalline deposit of metallic gold. A study of the magnetic susceptibilities of the original brown gold, the crystalline gold obtained by solution, and the residual gold leads to the conclusion that from brown gold, which is regarded as a mixture of  $\alpha$ - and  $\beta$ -gold, pure  $\beta$ -gold (crystalline gold) may be prepared by treatment with a solution of gold chloride,  $\alpha$ -gold being left as a residue.

The Future of Motor Spirit. V. B. Lewes. (Chem. World, ii, 111.)—The imports of petrol into Great Britain have increased from 18.000,000 gallons in 1905 to 80,000,000 gallons in 1912, while the world's production of crude oil has only increased from 28,500,000 to 50,000,000 tons. The principal sources of petrol imported in 1912 were the Dutch East Indies and America, which sent 46,000,000 and 16,000,000 gallons respectively. The surplus available for export from America is decreasing, and the excess of demand over supply has raised the price of crude oil at the oil fields. There are methods available for increasing the yield of petrol from crude oil. By compressing the gas which escapes from the oil wells a light spirit is recovered which may be mixed with the fractions of higher boiling-point. The petrol used for motor spirit has a specific gravity of 0.72 or higher, as compared with 0.68 when the supply was greater than the demand. The heavier fractions of crude oil may be converted into light oils by distillation in contact with catalysts such as nickel, or by "cracking." One process consists in spraying "solar oil" (a heavy fraction from American petroleum) with water into long iron retorts packed with iron filings and heated to 600° C. and condensing the vapors obtained fractionally; 100 gallons of "solar oil" yield 39 gallons of petrol, 13 gallons of solvent spirit, and 13 gallons of "varnish." Crude oil cannot be a lasting source of supply of motor spirit. The quantity of motor spirit (benzol, etc.) available from gas works in England at present is only 50,000 gallons per annum, and 8,000,000 gallons of benzol are recovered in coke-oven plants, which only treat 42 per cent. of the coal used for making metallurgical coke. The Scotch shale oil industry yields about 600,000 gallons of motor spirit annually. The motor spirit of the future will probably be alcohol, mixed with about 10 per cent. of benzol.

Electrolytic Theory of the Corrosion of Iron. B. Lambert. (Faraday Socy., April 4, 1913.)—Having already shown that water and oxygen are the only essentials to effect the rusting of iron, the author supports the electrolytic theory of corrosion and attributes the formation of rust to combination of the ferrous ions with the hydroxyl ions.

Radioactive Disintegration Products. A. FLECK. (Chem. Soc. Trans., ciii, 381.)—Fleck finds that uranium-X and radioactinium are chemically similar to, and non-separable from, thorium; mesothorium-2, non-separable from actinium; thorium-B is non-separable from lead; radium-B and actinium-B are very similar to lead, and probably non-separable from it; thorium-C, radium-C, and actinium-C are very closely allied to bismuth, and probably non-separable from it; radium-E is chemically identical with bismuth. Direct measurement of the development of radium-F from radium-E has confirmed the view that there is only one product (radium-E) between radio-lead and polonium.

Solar Energy and its Utilization. Anon. (Amer. Mach., xxxviii, 20, 824.)—James O. Handy gave the following statement before the Engineers' Society of Western Pennsylvania: In the tropics, assuming the solar constant at 1800 calories per hour per square metre, it is easily seen that the heat per square kilometre will be equal to that produced by the combustion of 1000 tons of coal. A surface of only 10,000 square kilometres receives in a year, calculating a day of only 6 hours, a quantity of heat corresponding to that produced by burning 3,500,000,000 tons of coal, or more than three times the annual production of coal. Desert of Sahara, with its area of 6,000,000 square kilometres, receives daily solar energy equivalent to 6,000,000,000 tons of coal. It is estimated that as a result of the sun's rays and the presence of moisture and carbon dioxide, etc., in the earth's crust and in the air the earth produces yearly 32,000,000,000 tons of vegetable matter, which, when burned, would correspond to 18,000,000 tons Thus the exhaustion of coal can be prepared for by studying which types of vegetation produce woody fibre most rapidly, and we can use intensive and extensive methods of cultivating them for fuel, and afterward convert this fuel into energy in the most economic way. There is reason for hope, however, that we may be able to do more than to improve agricultural methods of producing fuel, if we take advantage of the fact that many chemical changes are produced by the action of the sun's rays, and that some of these now known, or which may be discovered, may be the basis of a method of converting the sun's energy in dry, tropical countries quite directly into a form which may be transmitted to habitable countries where it may be used.

Aluminum Transmission Lines. Anon. (Eng., xcv, No. 2455, 86.)—The British Aluminum Company, Limited, of 109 Queen Victoria Street, London, E. C., has published a pamphlet dealing in considerable detail with the use of aluminum for overhead electric transmission lines. It states the general conditions, determines the design of transmission lines, gives a large amount of technical information for both copper and aluminum, from the transmission line point of view, and makes out a strong case for aluminum. This information covers comparative figures for conductivity, weight, tensile strength, temperature resistance effect, and expansion coefficients for the two materials. Questions of deflection and stress, jointing, the losses on lines, etc., are also dealt with, and the official standards for overhead line construction of various countries are given. This work should be consulted by all concerned with actual or projected overhead transmission work.

Weight Efficiency of Electric Motors and Prime Movers. W. B. Hird. (Inst. Elect. Engin. Journ., xlix, 620.)—An interesting paper which covers these subjects: The comparison of weight efficiencies of electric motors and of different types of prime movers: the choice of the unit for comparison; the general law connecting weight and output adopted as a working hypothesis; graphs embodying the results of investigations on steam engines, steam turbines, gas engines, oil engines, petrol engines, water turbines, and electric motors. The original paper will repay the perusal of those interested, especially the numerous curves and diagrams, and the table showing the "horsepower per revolution per ton of material" for the various kinds of prime movers.

Solubility of Radium Emanation in Water. M. Kofler. (Monatsh. Chem., xxxiv, 389.)—The values for the solubility of the radium emanation in distilled water at various temperatures (i.e., the equilibrium ratio of the emanation concentration in the liquid phase to that in the gaseous phase) are as follows:

Temp.	Solubility	Temp.	Solubility
0.5° C.	0.526	60° C.	0.127
17.5° C.	0.283	74° C.	0.112
35.0° C.	0.185	79° C.	0.111
41.0° C.	0.161	82° C.	0.111
51.0° C.	0.138	91° C.	0.108

The temperature coefficient is of the same order of magnitude as for other gases, decreasing with increase of temperature, and above 70° C. the solubility is constant within the limits of experimental error; but no minimum is shown on the solubility curve, as is the case with helium and hydrogen, although such minima might be expected with gases generally, from theoretical considerations.

Temperatures of the Decomposition of Carbonates. K. Friedrich. (Centralbl. f. Mineralogie, 1912, 616, 651, 684.)—A number of pure mineral carbonates in the form of fine powder were submitted to the heating action of an electric current, which was regulated so as to raise each specimen to a temperature of 1130° C. within an hour. The periods of time during which the heating continued, and the corresponding temperatures, were plotted on curves, which indicated for each substance the point when absorption of heat began and the point at which it reached a maximum. The first indicated the temperature of incipient dissociation (a) and the other the temperature of maximum decomposition (b), in all cases except those of strontium and barium carbonates, which were found to undergo molecular transformations at temperatures of about 300° C. below their temperature of decomposition. The values of (a) and (b) for different minerals are:

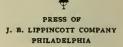
Catalytic Action of Mercury in Nitrations. R. Wolffenstein and O. Böters. (Ber., xlvi, 586.)—When concentrated nitric acid, or a mixture of nitric and sulphuric acids, acts on benzene in presence of mercuric nitrate, nitro-benzene only is yielded; while if nitric acid of lower concentration is used it acts in the first place as an oxidizing agent, and as a final product yields nitrophenols. A mixture of 100 grammes benzene, 800 grammes nitric acid of specific gravity 1.31, and 15 grammes of mercuric nitrate was heated on the water-bath under a reflux condenser with vigorous stirring. Nitrous gases were evolved, and the residue after cooling yielded a crystalline mass of 1.2.4-dinitrophenol and picric acid, i.e., the same products that are obtained by the direct nitration of phenol. Benzene derivatives react in an analogous manner. Oxides of nitrogen or nitrous acid may be used in place of nitric acid. 1.2.4-dinitrophenol in an almost pure state may be prepared directly from benzene by either of the following methods: (1) 120 grammes of benzene are mixed with 20 grammes of mercuric nitrate and the mixture treated with 270 grammes of nitrogen tetroxide and allowed to stand for some days at ordinary temperature. (2) 120 grammes of benzene are treated with 10 grammes of mercuric nitrate and 500 grammes of 50 per cent. nitric acid, 50 grammes of nitric oxide are added, and the mixture is stirred and heated to 50° C.

Illuminating Engineering Society.—The annual convention of the society will be held in Pittsburgh, Pa., beginning September 22,

An interesting programme is being prepared, which will include the usual number of social events, excursion trips, and visits to

industrial establishments in or near Pittsburgh.

The Mode of Combustion of Carbon. T. F. E. RHEAD and R. V. Wheeler. (Chem. Soc. Proc., xxix, 51.)—The authors have shown that carbon dioxide and carbon monoxide are produced together when carbon is burned, and now they give experiments to show how this simultaneous production of the two oxides occurs. Carbon, at all temperatures up to 900° C. and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it does not appear as oxygen, but as carbon dioxide and monoxide. The proportions of these two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen fixation. This "fixation" cannot be accounted for by any physical explanation; in all probability it is the outcome of a physico-chemical attraction between carbon and oxygen: physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which indeed exhibits progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means. When the complex is decomposed by heat, carbon dioxide and monoxide are produced. At a given temperature of decomposition these oxides make their appearance in a given ratio. Further, when a rapid stream of air at a given temperature is passed over carbon (which has been previously saturated with oxygen at that temperature), carbon dioxide and monoxide appear in the products of combustion in nearly the same ratio as they do in the products of decomposition of the complex at that temperature. It is therefore suggested that the first product of combustion of carbon is a loosely-formed physico-chemical complex which can be regarded as an unmistakable compound of carbon and oxygen of an, at present, unknown formula, CxOy. It is probable that no definite formula can be assigned to this complex.



# JOURNAL

OF

# THE FRANKLIN INSTITUTE

DEVOTED TO SCIENCE AND THE MECHANIC ARTS

Vol. CLXXVI

AUGUST, 1913

No. 2

VOLCANIC DUST AND OTHER FACTORS IN THE PRO-DUCTION OF CLIMATIC CHANGES, AND THEIR POSSIBLE RELATION TO ICE AGES.\*

BY

#### W. J. HUMPHREYS, C.E., Ph.D.,

Professor of Meteorological Physics, U.S. Weather Bureau, and George Washington University

#### INTRODUCTION.

OLD lake beaches, glacial moraines, and various other geological records give indisputable evidence of numerous climatic changes. It appears, too, that these changes were irregular in their times of occurrence and irregular also in their intensity and duration. Many seem to have been mild and relatively fleeting, while a few were so profound and lasting as even to bring on ice ages and to cover extensive areas of the earth with glacial sheets, or, on the other hand, to melt these sheets away and to establish for long periods warm and genial climates over much the greater portion of the earth.

When this series of climatic changes began there is no sure means of knowing, for the records, especially those of glacial origin, grow gradually fainter and more scanty with increase

<sup>\*</sup> Developed from an outline presented before the Astronomical and Astrophysical Society of America, at Cleveland, Ohio, January 1, 1913. Communicated by the author.

<sup>[</sup>Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.]

Copyright, 1913, by The Franklin Institute. Vol. CLXXVI, No. 1052—10

of geologic age, and it is probable, therefore, that the effects of many of the earlier changes have long since been completely obliterated. But, however this may be, it is well-nigh certain that from the time of the earliest known of these changes down to the very present the series has been irregularly continuous, and the end, one might reasonably assume, is not yet. Change after change of climate in an almost endless succession, and even additional ice ages, presumably are still to be experienced, though, except small and fleeting changes to be noted below, when they shall begin, how intense they may be, or how long they shall last no one can form the slightest idea.

Numerous attempts, some of them invoking purely terrestrial and others extra-terrestrial or cosmical conditions, have been made to find a probable and at the same time an adequate physical basis for or cause of the known climatic changes of the distant past, and especially for those profound climatic changes that brought about the extensive glaciation that prevailed during the so-called ice ages; but nearly all the older suggestions have been definitely and finally abandoned, either because of inconsistency with known physical laws or abandoned because they are inadequate to meet the conditions imposed upon them by the results of geological investigations.

#### FACTS OF CLIMATIC CHANGES.

Among the more important facts with respect to climatic changes that appear to have been established, and which presumably, therefore, must be met by any theory that would account for such changes, or explain specifically the origin of ice ages, are the following:

- (a) The climatic changes were several, probably many.
- (b) They were simultaneous over the entire earth, and in the same sense; that is, colder everywhere at the same time (climatically speaking) or warmer everywhere.
  - (c) They were of unequal intensity.
- (d) They probably were of irregular occurrence and of unequal duration.
- (e) They, at least one or more, progressed with secondary variations of intensity, or with advances and retreats of the glacial edge.
  - (f) They have occurred from very early, probably from the

earliest, geological ages down to the present, and presumably will continue irregularly to recur for many ages yet to come.

#### PRINCIPAL ICE-AGE THEORIES.

It would be easy to catalogue perhaps a score of more or less rational hypotheses in regard to the origin of the ice ages, and doubtless even a larger number that are quite too absurd ever to have received serious consideration, and to point out in each case the known and the suspected elements of weakness. But this would only be a repetition of what, in part at least, has often been done before and therefore could serve no good purpose.

As already stated, only a few of these hypotheses still survive, nor do all of even these few really merit the following they have. Apparently those which still claim each a large number

of adherents are, respectively:

(a) Croll's Eccentricity Theory.\* This is based on the assumption that when the earth's orbit is most eccentric, or when the earth's maximum solar distance differs most from its minimum solar distance, ice will accumulate to a great extent over that half of the globe which has its winter during aphelion.

For some time Croll's theory was very generally accepted, and it seems still to have many adherents, despite the destructive

criticisms of Newcomb 1 and Culverwell.2

The chief objections to Croll's theory are:

- 1. That the assumption that midwinter and midsummer temperatures are directly proportional to the sun's heat at these times is not at all in accord with observed facts.
- 2. That each ice age would be limited to a fraction of the precessional period, 21,000 years, which, according to most geologists, is too short a time. In fact, it is already longer than this whole period, according to the best evidence, since the culmination of the last ice age.
- 3. That the successive ice ages would have occurred alternately in the northern and southern hemispheres, instead of, as generally believed to have been the case, in both hemispheres simultaneously.

<sup>2</sup> Phil. Mag., 38, p. 541, 1894.

<sup>\*</sup> Phil. Mag., 28, p. 121, 1864, and elsewhere.

<sup>&</sup>lt;sup>1</sup> Amer. Jr. Sci., 11, p. 263, 1876; Phil. Mag., 17, p. 142, 1884.

(b) The Carbon Dioxide Theory. This theory, advocated by Tyndall,<sup>3</sup> Arrhenius,<sup>4</sup> Chamberlain,<sup>5</sup> and others, is based on the selective absorption of carbon dioxide for radiation of different wave-lengths, and on its assumed variation in amount.

It is true that carbon dioxide is more absorptive of terrestrial than of solar radiations, and that it therefore produces a green-house or blanketing effect, and it is also probably true that its amount in the atmosphere has varied through appreciable ranges as a result of volcanic additions on the one hand, and of oceanic absorption and chemical combination on the other. But it is not possible to say exactly how great an effect a given change in the amount of carbon dioxide in the atmosphere would have on the temperature of the earth. However, by bringing a number of known facts to bear on the subject it seems possible to reach approximate conclusions. Thus from the experiments of Schlaefer 6 we know that at atmospheric pressure a column of carbon dioxide 50 centimetres long is ample for maximum absorption, since one of this length absorbs quite as completely as does a column 200 centimetres long at the same density. Also from the experiments of Angström<sup>7</sup> and from those of E. v. Bahr 8 we know that the absorption of radiation by carbon dioxide or other gas increases with increase of pressure, and, what is of great importance, that both qualitatively and quantitatively this increase of absorption is exactly the same whether the given higher pressure be obtained by compression or by the addition of an inert gas.

Now the amount of carbon dioxide in the atmosphere is equivalent to a column of the pure gas, at ordinary room temperature and atmospheric pressure, of, roughly, 250 centimetres in length. Hence, according to the experiments just described of Angström and E. v. Bahr, the carbon dioxide now in the atmosphere must absorb radiation very approximately as would a column 475 centimetres long of the pure gas at its average barometric pressure of, say, 400 millimetres. But Schlaefer's experiments above referred to show that such a column would

<sup>&</sup>lt;sup>3</sup> Phil. Mag., 22, p. 277, 1861.

<sup>\*</sup> Phil. Mag., 41, p. 237, 1896.

<sup>&</sup>lt;sup>5</sup> Jr. Geol., 7, p. 545, 1899.

<sup>&</sup>lt;sup>6</sup> Ann. der Phys., vol. 16, p. 93, 1905. <sup>7</sup> Arkiv för Matematik, Astronomi och Fysik, vol. 4, No. 30, 1908.

<sup>8</sup> Ann. der Phys., vol. 29, p. 780, 1909.

be just as effective as one two or three times this length, and, on the other hand, no more effective than a column one-half or one-fourth as long.

Hence, finally, doubling or halving the amount of carbon dioxide now in the atmosphere, since this would make but little difference in the total pressure, would not appreciably affect the amount of radiation actually absorbed by it, whether of terrestrial or of solar origin.

Again, as already explained by Abbot and Fowle, the water vapor always present in the atmosphere leaves, because of its high coefficients of absorption in substantially the same regions where carbon dioxide is effective, but little radiation for the latter to take up. Hence, for this reason, too, as well as for the one given above, either doubling or halving the present amount of carbon dioxide could alter but little the total amount of radiation actually absorbed by the atmosphere, and therefore, seemingly, could not appreciably change the average temperature of the earth, or be at all effective in the production of marked climatic changes.

Nevertheless, in spite of both the above objections, there appears to be at least one way by which a change, especially if a decrease, in the amount of carbon dioxide in the atmosphere might affect temperatures at the surface of the earth, so that we are not yet in position to say that no such change was ever an appreciable factor in the production of an ice age.

Further discussion of this particular point will be taken up later, after the introduction of certain observational evidence that seems to bear on the subject.

We will now return to the existing ice-age theories and consider briefly just two more before coming to the main body of the paper.

(c) The Solar Variation Theory. This is based on the assumption that the solar radiation has waxed and waned, either cyclically or irregularly, through considerable ranges and over long intervals of time.

This theory is seductively attractive,—it looks so simple, so sufficient, and so safe from attack. But if impossible to disprove, it is equally difficult to establish, and therefore it should conditionally be put aside, held in reserve, as it were, as a last

<sup>&</sup>lt;sup>9</sup> Annals of the Astrophysical Observatory, Smithsonian Institution, vol. 2, p. 172, 1908.

resort, in favor of a more complete search for and examination of other possible causes, for, after all, the supposed solar changes, for which we can assign no probable cause or causes,

may never have happened.

(d) The Elevation Theory. This theory assumes the simultaneous (geologically speaking) rise or fall of many, possibly all, land areas through a range that may have amounted to several thousand feet. It is argued that such movements would account for not only the phenomena of the ice ages, but also for, among other things, the many suboceanic canyons, such as that of the Hudson, the St. Lawrence, the Congo, and others.

This theory is mentioned here not because of the number of supporters it has at present, for obviously this number is not large, but because any such changes in elevation that it supposes, whether local or general, if they ever took place—and apparently great changes in elevation have occurred—must have affected the climates of the regions that so moved, and therefore must have been a factor—no one knows how great—in the production of at least regional, if not world-wide, climatic changes of the past.

These three theories, then, omitting d, which but few support, of the origin of the ice ages, namely: The eccentricity theory, the carbon dioxide theory, and the solar variation theory, are the only ones that at present appear to have many adherents, and even these few seem more likely to lose than to gain in number and strength of defenders. The first has failed utterly under searching criticism; the second has been sadly impaired; while the third, provokingly secure from all tests, is strong only as and to the extent that other theories are disproved or shown to be improbable.

The above introduction brings us to the essential purpose of this paper, to the discussion of a factor in the production of climatic changes including, possibly, even those great changes incident to the advance and retreat to maximum and minimum of glaciation. It may not have been the chief cause of our greatest climatic changes, or even a large contributing factor, but nevertheless a factor, possibly of large size, and therefore worthy of consideration.

The factor in question is

#### VOLCANIC DUST IN THE UPPER ATMOSPHERE.

After the outline of the following discussion had taken shape it was found, on looking up the appropriate literature, that the brothers P. and F. Sarasin <sup>10</sup> had suggested, a number of years ago, that the low temperature essential to the glaciation of ice ages was caused by the absorption of solar radiation by high volcanic dust-clouds.

But the idea that dust of this nature, when scattered through the atmosphere, may lower the temperature of the surface of the earth was already old, having been advanced at a much earlier date,—in fact, long before even the existence of ice ages had been suspected, much less attempts made to find their cause. Thus in May, 1784, Benjamin Franklin (and he may not have been the first) wrote as follows:

During several of the summer months of the year 1783, when the effects of the sun's rays to heat the earth in these northern regions should have been the greatest, there existed a constant fog over all Europe, and great part of North America. This fog was of a permanent nature; it was dry, and the rays of the sun seemed to have little effect toward dissipating it, as they easily do a moist fog, arising from water. They were indeed rendered so faint in passing through it that, when collected in the focus of a burning-glass, they would scarce kindle brown paper. Of course, their summer effect in heating the earth was exceedingly diminished.

Hence the surface was early frozen.

Hence the first snows remained on it unmelted, and received continual additions.

Hence perhaps the winter of 1783-4 was more severe than any that happened for many years.

The cause of this universal fog is not yet ascertained. Whether it was adventitious to this earth, and merely a smoke proceeding from the consumption by fire of some of those great burning balls or globes which we happen to meet with in our course round the sun, and which are sometimes seen to kindle and be destroyed in passing our atmosphere, and whose smoke might be attracted and retained by our earth; or whether it was the vast quantity of smoke, long continuing to issue during the summer from Hecla, in Iceland, and that other volcano which arose out of the sea near that island, which smoke might be spread by various winds over the northern part of the world, is yet uncertain.

It seems, however, worth the inquiry, whether other hard winters, recorded in history, were preceded by similar permanent and widely-extended summer fogs. Because, if found to be so, men might from such fogs con-

<sup>&</sup>lt;sup>10</sup> Verhandlungen der Naturforschenden Gesellschaft in Basel, vol. 13, p. 603, 1901.

Vol. CLXXVI, No. 1052—11

jecture the probability of a succeeding hard winter, and of the damage to be expected by the breaking up of frozen rivers in the spring; and take such measures as are possible and practicable to secure themselves and effects from the mischiefs that attend the last.<sup>11</sup>

The idea, then, that volcanic dust may be an important factor in the production of climatic changes is not new, though just how it can be so apparently has not been explained, nor has the idea been specificially supported by direct observations. This is not to be taken as a criticism of the above-mentioned pioneer paper by the brothers Sarasin, for indeed the arguments, now easy, were at that time impossible, because the observations upon which they largely are based had not then been made. Indeed the absorption of radiation by volcanic dust, by which they supposed the earth's temperature to be lowered, can now be shown to be, of itself alone, not only insufficient, but even productive, in all probability, of the opposite effect—of a warming instead of a cooling of the earth's surface.

To make this point clear: Consider a thin shell of dust about the earth and let I be the average intensity of the normal component of solar radiation on it. Further, let a be the dust's coefficient of absorption for solar radiation, independent, presumably, of intensity, and b its coefficient of absorption for terrestrial radiation. Obviously, in the case of equilibrium, all the energy absorbed by the dust is radiated away; half of it, very approximately, to the earth and half of it to space. Hence, starting with I as the solar radiation normally incident, per unit area and unit time, upon the dust layer, we have, if there is no reflection and no scattering,

aI = rate of absorption of solar radiation.

 $I(\mathbf{1} - a) = \text{intensity of solar radiation reaching earth, or lower atmosphere.}$ 

 $\frac{1}{2}\,aI=$  intensity of dust radiation, resulting from above absorption, reaching earth.

Summing these two radiations incident upon the earth, we have

$$I(1-a) + \frac{1}{2}aI = I\left(1 - \frac{a}{2}\right).$$

Eventually, when equilibrium is established, the earth must lose the same amount of radiation that it gains, though, of

<sup>&</sup>lt;sup>11</sup> See Sparks's "Life of Benjamin Franklin," vol. 6, 455-457 (cited in Proceedings of the Amer. Phil. Soc., vol. 45, p. 127, 1906).

course, chiefly through a different spectral region, and therefore, after a time, assuming the earth to absorb all incident radiation,

 $I\left(1-\frac{a}{2}\right)$  = the intensity of the outgoing as well as that of the incoming radiation.

Of this the dust absorbs, per unit area and unit time,

$$bI\left(1-\frac{a}{2}\right)$$
,

of which, in turn, one half is radiated to space and one half back to earth, there to be reabsorbed and again radiated. The intensity of the normal radiation now reaching the earth is

$$I\left(1-\frac{a}{2}\right)+\frac{b}{2}I\left(1-\frac{a}{2}\right),$$

of which the second term becomes, after a time, the increase in the intensity of the outgoing radiation. Hence, after further absorption and re-radiation by the dust layer, the next increment of radiation to the earth is

$$\left(\frac{b}{2}\right)^2 I\left(1-\frac{a}{2}\right),$$

and so on indefinitely.

In the end, then, when the ultimate equilibrium is attained, the intensity of the total normal radiation reaching the earth,  $I_e$ , is given by the equation,

$$I_{\epsilon} = I\left(1 - \frac{a}{2}\right) \left\{1 + \frac{b}{2} + \left(\frac{b}{2}\right)^{2} + \dots + \left(\frac{b}{2}\right)^{\infty}\right\}$$
or  $I_{\epsilon} = I\left\{1 + k(b - a)\right\}\dots$  (A).

in which

$$k = \frac{1}{2} \left\{ 1 + \frac{b}{2} + \left(\frac{b}{2}\right)^2 + \dots + \left(\frac{b}{2}\right)^{\infty} \right\}.$$

Now b is positive, and therefore k is also positive. Hence

$$I\left\{\mathbf{1}+k\;(b-a)\right\} \stackrel{\geq}{=} I,$$

according as 
$$b \stackrel{\geq}{=} a$$
.

That is to say, the total amount of radiation reaching the earth is increased, unchanged, or decreased by the surrounding dust layer according as the dust's coefficient of absorption of terrestrial radiation is greater than, equal to, or less than its coefficient of absorption of solar radiation.

Now in the case of many, if not all, rocky materials, such as make up the particles of volcanic dust, the coefficient of absorption is much greater for terrestrial radiation than for solar radiation, 12 or, in terms of the above symbols, in the case of volcanic dust b is greater than a. Hence, so far as mere absorption of radiation is concerned, the only action mentioned by the brothers Sarasin, a veil of volcanic dust, in all probability, would slightly *increase* and not decrease, as they supposed, the average temperature of the earth.

But, then, absorption is not the only effect of a dust veil on radiation; reflection and scattering both are important and must

be fully considered.

These actions, however, reflection and scattering, depend fundamentally upon the ratio of the linear dimensions of the particles concerned to the wave-length of the incident radiation, and therefore, before undertaking to discuss them in this connection, it will be essential to determine the approximate size of the individual grains of floating volcanic dust, and also the average wave-lengths, weighted according to energy, of solar and of terrestrial radiation. It will be desirable, also, to consider whether or not, and if so how, dust of any kind can remain long suspended in the atmosphere. And this point will be examined first, since, obviously, the longer the dust can float the more important, climatically, it may have been in the past and in the future may again become.

Atmospheric Regions.—The atmosphere is divisible into the stratosphere and the troposphere; or the isothermal region and the convective region; or, in other words, the region, in middle latitudes, at and beyond about 11 kilometres above sea level where, being free from vertical convection, ordinary clouds never form and the turbulent, stormy region below this level which is frequently swept by clouds and washed by snow and rain. The

<sup>&</sup>lt;sup>12</sup> Coblentz, Publications of Carnegie Institution of Washington, Nos. 65 and 97.

physical reason for or cause of the existence of the isothermal region is well known,13 and is such that we feel quite sure that ever since the earth was warmed by solar radiation, as at present, rather than by internal heat, the temperature of its atmosphere beyond a certain level, whatever its composition, must have varied but little, as it now varies but little, with change of altitude, and therefore that this region must then have been free, as it now is free, from clouds and condensation. Obviously, then, in the past, as in the present, and as it must continue to be so long as the earth shall have an atmosphere, any volcanic or other dust, that by whatever process was gotten into and distributed through the isothermal region where there were no clouds or other condensation to wash it out, must have drifted about till gravity, overcoming the viscosity of the atmosphere, by slow degrees pulled it down to the region of clouds and storms. How long such a process must take depends, of course, upon a number of things, among which the size of the particles is vitally important. And this brings us to the next consideration.

Size of Volcanic Dust Particles.—For two or three years after the eruption of Krakatoa, in 1883, also after the eruptions of Mount Pelée and Santa Maria, in 1902, and again after the eruption of Katmai, in 1912, a sort of reddish-brown corona was often, under favorable conditions, observed around the sun. It was 10 degrees to 12 degrees wide, and had an angular radius, to the outer edge, of 22 degrees to 23 degrees. This phenomenon, known as Bishop's ring, clearly was a result of diffraction of sunlight by the particles of volcanic dust in the upper atmosphere, and therefore furnished a satisfactory means for determining the approximate size of the particles themselves. The subject has been rather fully discussed by Pernter, who finds the diameter of the particles, assuming them spherical, to be approximately 185 × 10<sup>-6</sup> cm., or 1.85 microns. The equation used has the form

$$r = \frac{m}{\pi} \frac{\lambda}{\sin \vartheta}$$

in which r is the radius of the dust particle,  $\lambda$  the wave-length of the diffracted light (here taken as  $571 \times 10^{-7}$  cm., or 0.571

<sup>&</sup>lt;sup>13</sup> Humphreys, *Astrophys. Jr.*, 29, p. 14, 1909.

Gold, Proc. Roy. Soc., Series A, 82, p. 43, 1909.

<sup>14</sup> Met. Zeit., 6, p. 401, 1889.

micron),  $\vartheta$  the angular radius of the ring, and m a numerical term which for the outer edge of the ring, and successive minima, has the approximate values,

$$\frac{\pi}{2} (n + 0.22),$$

in which n = 1,2,3,-, respectively.

Now, since the width and angular dimensions of Bishop's ring, as seen at different times and under different circumstances, have varied but little, the above value, 1.85 microns, may provisionally be assumed to be the average diameter of those particles of volcanic dust that remain long suspended in the atmosphere.

Time of Fall.—The steady or terminal velocity of a sphere falling in a fluid, assuming no slip between fluid and sphere, is

given by Stokes's 15 equation:

$$V = \frac{2}{9} g r^2 \frac{(\sigma - \rho)}{\mu},$$

in which V is the velocity of the fall, g the acceleration of gravity, r the radius of the sphere,  $\sigma$  the density of the sphere,  $\rho$  the density of the fluid, and  $\mu$  its viscosity.

However, there always is slip, so that the actual velocity of fall is, according to Cunningham, 16

$$V = \frac{2}{9}gr^2\frac{(\sigma-\rho)}{\mu}\left(l+A\frac{l}{r}\right),$$

in which l is the free path of the gas molecules, A a constant, and the other symbols as above explained.

Obviously *l*, other things being equal, is inversely proportional to the gas density, or pressure, if temperature is constant. Hence

$$V = \frac{2}{9} gr^2 \frac{(\sigma - \rho)}{\mu} \left( l + \frac{B}{rp} \right) - - - (1).$$

in which B is a constant for any given temperature, p the gas pressure, or, if preferred, barometric height.

Now a series of valuable experiments by McKeehan <sup>17</sup> has shown that for  $21^{\circ}$  C., and when p is the pressure in terms of millimetres of mercury,

$$B = .0075 \pm 3.$$

<sup>15</sup> Math. and Phys. Papers, vol. 3, p. 59.

<sup>&</sup>lt;sup>16</sup> Proc. Roy. Soc., 83 A, p. 357, 1910.

<sup>&</sup>lt;sup>17</sup> Phys. Rev., 33, p. 153, 1911.

The value of  $\mu$ , for dry air, is also closely known from the careful work of Breiterbach, <sup>18</sup> Schultze, <sup>19</sup> and Fischer, <sup>20</sup> all of whom obtained substantially the same values. At 26° C., as computed by Millikan <sup>21</sup> from the results obtained by these observers,

$$\mu = 1863 \times 10^{-7}$$
.

Therefore, remembering that  $\mu$  varies as the square root of the absolute temperature, it is easy to compute, by the aid of equation (1), the velocity of fall of volcanic dust, assuming gravity to be the only driving force. There is, of course, radiation pressure, both toward and from the earth, as well as slight convective and other disturbances, but presumably gravitation exerts the controlling influence.

The following table of approximate velocities and times of fall for volcanic dust was computed by substituting in equation (1) the given numerical values, namely:

 $g = 981 \frac{\text{cm.}}{\text{sec.}}$ 

r = .000092 cm.

 $\sigma = 2.3$ , approximate density of Krakatoa dust.

 $\rho = 0$ , being negligible relative to  $\sigma$ .

 $\mu = 1760 \times 10^{-7}$ , appropriate to  $-55^{\circ}$  C., roughly the temperature, in middle latitudes, of the isothermal region.

B = .0056, appropriate to  $-55^{\circ}$  C. p = millimetres barometric pressure.

## Velocity and time of fall.

Height in kilometres	Barometric pressure <sup>22</sup>	Centimetres per second	Seconds per centimetre
40	1.84	0.82173	1.2170
30	8.63	0.19419	5.2695
20	40.99	0.05992	16.690
15	89.66	0.04048	24.703
11*	168.00	0.03280	30.44
0	760.00	0.02522†	39.65†

<sup>\*</sup>Isothermal level of middle latitudes.

According to this table it appears that spherical grains of sand of the size assumed, 1.85 microns in diameter, would re-

<sup>†</sup> Temperature 21° C.

<sup>18</sup> Ann. der Phys., 5, p. 168, 1901.

<sup>19</sup> Ann. der Phys., 5, p. 557, 1901.

<sup>&</sup>lt;sup>20</sup> Phys. Rev., 28, p. 104, 1909.

<sup>21</sup> Phil. Mag., 19, p. 215, 1910.

<sup>22</sup> Humphreys, Journal of The Franklin Institute, 165, p. 215, 1913.

quire more than one year to fall from only that elevation already reached by balloons, 37.7 kilometres, down to the under surface of the isothermal region, at the height of 11 kilometres.

As a matter of fact, volcanic dust, at least much of it, consists of thin-shelled bubbles or fine fragments of bubbles, and therefore must settle much slower than solid spheres, the kind above assumed. Indeed, the finest dust from Krakatoa, which reached a great altitude, probably not less than 40 nor more than 80 kilometres, was from two and a half to three years in reaching the earth, or, presumably, as above explained, the upper cloud levels.

At any rate, volcanic dust is so fine, and the upper atmosphere above 11 kilometres so free from moisture and vertical convection, that once such dust is thrown into this region, as it obviously was by the explosions of Skaptar Jökull and Asamayama in 1783, Babuyan in 1831, Krakatoa in 1883, Santa Maria and Pelée in 1902, Katmai in 1912, and many others, it must require, as a rule, because of its slow descent, from one to three years to get back to the earth. And this clearly has always been the case since the earth first assumed substantially its present condition, or had a cool crust and a gaseous envelope.

Obviously, then, we have only to determine the present action of such dust on incoming solar and outgoing terrestrial radiation in order to reach a logical deduction as to what its effect on climate must have been if, through extensive volcanic activity, it ever for a long or even considerable term of years more or less continuously filled the upper atmosphere, as conceivably may have happened. And the same conclusion in regard to the possible effect of dust on the climates of the past clearly applies with equal force to the climates of the future.

Action of Dust on Solar Radiation.—Since solar radiation at the point of maximum intensity  $^{23}$  has a wave-length less than  $5 \times 10^{-5}$  cm., or half a micron, and since fully three-fourths of the total solar energy belongs to spectral regions whose wavelengths are less than  $10^{-4}$  cm., or one micron, it follows that the cubes of solar wave-lengths must, on the whole, be regarded as small in comparison with the volume of a volcanic dust particle—the diameter of which, as we have seen, is nearly 2 microns.

<sup>&</sup>lt;sup>23</sup> Abbot and Fowle, Annals Astrophys. Obsy., Smithsonian Inst., vol. 2, p. 104, 1908.

Hence, in discussing the action of volcanic dust on incoming solar radiation, we can, with more or less justification, assume the particles to be opaque through reflection or otherwise, and therefore use Rayleigh's <sup>24</sup> arguments as applied to a similar case.

Let r be the radius of the particle, n the number of particles per cubic centimetre, and a the projected joint area of these particles. Then, for random and sparsely-scattered particles,

$$a = n\pi r^2$$

Hence, on dividing a plane parallel to the wave front into Fresnel zones, we see that for each centimetre traversed the amplitude of the radiation is reduced in the ratio of 1 to 1— $n\pi$   $r^2$ , therefore, if A is the initial amplitude, and  $A_x$  the amplitude after passing through x centimetres of the uniformly dusty region, we have, assuming  $n\pi$   $r^2$  to be only a small fraction of a square centimetre,

$$A_x = A (I - n\pi r^2)^x = A e^{-n\pi r^2 x}$$

Further, if I is the initial and  $I_x$  the final intensity, then

$$I_x = Ie^{-2n\pi r^2 x}$$

Hence, in the case of volcanic dust, where, as already explained,  $r = 92 \times 10^{-6}$  centimetres,

$$A_r = Ae^{-n\pi x (92)^2 10^{-12}}$$

and

$$I_{x} = Ie^{-2n\pi x (92)^{2} IO^{-12}}$$

Presumably the particles of dust are not absolutely opaque and therefore  $I_x$  probably is a little larger than the value here given, though even so this value is at least a first approximation.

Action of Dust on Terrestrial Radiation.—Terrestrial radiation, at the point of maximum intensity, has a wave-length of, roughly, 12 × 10<sup>-4</sup> centimetres, and therefore the wave-lengths of nearly all outgoing radiation are large in comparison with the diameters of those volcanic dust particles that remain long suspended in the atmosphere. Hence, while such particles largely reflect solar radiation, as is obvious from the whiteness

<sup>&</sup>lt;sup>24</sup> Phil. Mag., 47, p. 375, 1899.

of the sky when filled by them, they can only scatter radiation from the earth, according to the laws first formulated by Rayleigh,<sup>25</sup> whose papers must be consulted by those who would fully understand the equations which here will be assumed and not derived.

Let E be the intensity of terrestrial radiation as it enters the dusty shell, or as it enters the isothermal region, and  $E_{\nu}$  its intensity after it has penetrated this region, supposed uniformly dusty, a distance y centimetres; then, remembering that the dust particles are supposed to be spherical, we have

 $E_y = Ee^{-hy}$ 

where

$$h = 24\pi^{3}n \frac{(K'-K)^{2}}{(K'+2K)^{2}} \frac{T^{2}}{\lambda^{4}},$$

in which n is the number of particles per cubic centimetre, K the dielectric constant of the medium, K' the dielectric constant of the material of the particles, T the volume of a single particle, and  $\lambda$  the wave-length of the radiation concerned.

But K = 1, and, since the dust seems generally to be a kind of a glass, it may not be far wrong to assume that K' = 7. Hence, with these values,

$$h = \prod_{n=1}^{3} n \frac{T^2}{\lambda^4}$$
, nearly.

Relative Action of Dust on Solar and Terrestrial Radiation.—To determine whether such a dust layer as the one under discussion will increase or decrease earth temperatures it is necessary to compare its action on short wave-length solar radiation with its action on long wave-length radiation from the earth.

In the case of solar radiation, as explained,

$$I_x = Ie^{-2n\pi x(92)^2 Io^{-12}}$$

Clearly, then, the intensity of the solar radiation is reduced in the ratio of 1 to e, or

$$I_x:I=1:e$$

when  $x = \frac{10^{12}}{2n\pi(92)^2}$  centimetres  $= \frac{188}{n}$  kilometres, approximately.

<sup>25</sup> Loc. cit.

On the other hand, in the case of terrestrial radiation, where

$$E_{y}=Ee^{-i\,\mathrm{i}\,\pi^{3}n}\,\frac{T^{2}}{\lambda^{4}}\,y,$$

the intensity is reduced in the ratio of 1:e, or

$$E_{v}: E = 1:e,$$

when

$$y = \frac{\lambda^4}{11\pi^3 n T^2}$$
 centimetres,

in which  $T = \frac{4}{3}\pi (92)^3 10^{-18}$ 

and  $\lambda = 12 \times 10^{-4}$ , the region of maximum intensity.

Hence

$$y = \frac{5700}{n}$$
 kilometres, approximately.

Therefore, finally,

$$y: x = 30: I$$
, roughly,

or the shell of volcanic dust, the particles all being the size given, is some thirty-fold more effective in shutting solar radiation out than it is in keeping terrestrial radiation in. In other words, the veil of dust produces an inverse green-house effect, and hence, if the dust veil were indefinitely maintained, the ultimate equilibrium temperature of the earth would be lower than it is when no such veil exists.

The ratio 30 to 1 in favor of terrestrial radiation in its ability to penetrate the dusty atmosphere may at first seem quite too large, but it should be remembered that the dust particles in question are to terrestrial radiation in general as air molecules are to solar radiation, in the sense that in both cases but little more than mere scattering takes place. Now it is obvious that the dust particles are many-fold more effective in intercepting solar radiation, which they appear to do chiefly by reflection, than are an equal number of air molecules which simply scatter it; and hence it may well be that the above theoretically-determined ratio, 30 to 1, is no larger than the ratio that actually exists, or, at any rate, that it is of the correct order.

It must be distinctly understood that certain of the assumptions upon which the foregoing is based, uniformity of size, complete opacity and sphericity of the dust particles, for instance, are only approximately correct, but they are the best

that at present can be made, and doubtless give at least the order of magnitude of the effects, which indeed, for the present

purpose, is quite sufficient.

It may be well, in this connection, to call attention to the fact that excessively fine dust particles, or particles whose diameters are half, or less, the wave-length of solar radiation (region of maximum intensity), and which therefore remain longest in suspension, shut out solar radiation many-fold more effectively than they hold back terrestrial radiation. This is because both radiations, solar and terrestrial, are simply scattered by such small particles, and scattered according to the inverse fourth power of the wave-length.

Now the ratio of solar wave-length to terrestrial wave-length (region of maximum intensity in both cases) is roughly 1 to 25, and therefore the ratio of their fourth powers as 1 to  $39 \times 10^4$ , about. Hence, in the case of the very finest and therefore most persistent dust, the interception of outgoing radiation is wholly negligible in comparison with the intercep-

tion of incoming solar radiation.

Let us next see what observational evidence, pyrheliometric or otherwise, we have bearing on the effect of volcanic dust on radiation.

Pyrheliometric Records.—Direct measurement of solar radiation by means of the pyrheliometer shows marked fluctuations from year to year in the intensity of this radiation as received at the surface of the earth. This subject has been carefully studied by Dr. H. H. Kimball,<sup>26</sup> of the United States Weather Bureau, and Fig. 1, kindly prepared by him for use in this article, graphically represents the course of pyrheliometric readings from the beginning of 1883 till and including April, 1913. The yearly values are given in terms of the average value for the entire period, and, therefore, percentages of this average do not represent the full effect of the disturbing causes, of which volcanic dust certainly is the chief.

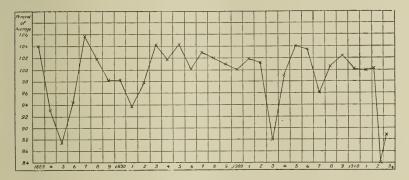
The marked decrease in the pyrheliometric readings for 1884, 1885, and 1886 doubtless were largely, if not almost wholly, due to the eruption of Krakatoa in the summer of 1883; the decreased values of 1888 to 1892 inclusive occurred during

<sup>&</sup>lt;sup>26</sup> Bull. Mt. Weather Obsy., 3, p. 69, 1910.

a period of exceptional volcanic activity, but were most probably due essentially to the violent eruptions of Bandaisan (1888), Bogoslof (1890), and Awoe, on Great Sangir (1892); the low values of 1903 to the eruptions of Santa Maria, Pelée, and Colima; and the present low values, 1912–1913, to the recent (1912) explosion of Katmai.

There is then abundant pyrheliometric evidence that volcanic dust in the upper atmosphere actually does produce that decrease in direct solar radiation that theory indicates it should, and,

Fig. 1.



Annual average pyrheliometric values.

as the theory is well founded and the observations carefully taken, this mutual confirmation may be regarded as conclusive both of the existence of volcanic dust in the upper atmosphere (isothermal region) and of its efficiency in intercepting direct radiation from the sun.

It should be remembered, however, in this connection, that the intensity of the solar radiation at the surface of the earth depends upon not only the dustiness of the earth's atmosphere, but also upon the dustiness, and, of course, the temperature, of the solar atmosphere.

Obviously, dust in the sun's envelope must more or less shut in solar radiation just as, and in the same manner that, dust in the earth's envelope shuts it out. Hence it follows that when this dust is greatest, other things being equal, the output of solar energy will be least, and that when the dust is least, other things being equal, the output of energy will be greatest.

Not only may the intensity of the emitted radiation vary because of changes in the transparency of the solar atmosphere, but also because of any variations in the temperature of the effective solar surface, which, it would seem, might well be hottest when most agitated, or at the times of spot maxima, and coolest when most quiescent, or at the times of spot minima.

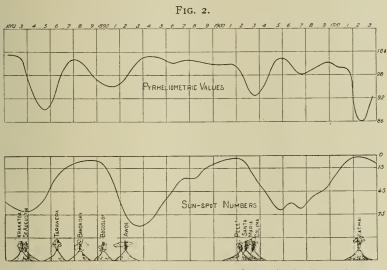
Now the dustiness of the solar atmosphere, manifesting itself as a corona, certainly does vary through a considerable range from a maximum when the sun-spots are most numerous to a minimum when they are fewest, and therefore, partly because of changes in the transparency of the solar envelope, and partly because of changes in the solar surface temperatures, if, as in all probability they do, such temperature changes take place, we should expect the solar constant also to vary from one value at the time of spot maximum to another at the time of spot minimum, and to vary as determined by the controlling factor, dust or temperature.

If the above reasoning is correct, it follows that pyrheliometric readings are functions of, among other things, both the solar atmosphere and our own terrestrial atmosphere; and as the former is altered chiefly by sun-spots or at least varies with their production and existence, and the latter by volcanic explosions, a means is at hand for comparing the relative importance of the two radiation screens.

Fig. 2 shows one such comparison. The upper curve gives smoothed annual average pyrheliometric readings (not solar constants, though closely proportional to them) and the lower curve sun-spot numbers. It will be noticed that in their most pronounced features the two curves have but little in common, and that the great drops in the pyrheliometric values occur simultaneously with violent volcanic explosions, as already explained, and not at the times of sun-spot changes. Hence it appears that the dust in our own atmosphere, and not the condition of the sun, is the controlling factor in determining the magnitudes and times of occurrence of great and abrupt changes of insolation intensity at the surface of the earth.

This is what the curves positively show, but it is not all they indicate. From 1894 to 1901 there were no volcanic explosions, so far as known, of importance, and therefore during this time the upper atmosphere must have been more or less uniformly

free from dust. But there seems to have been, during this interval, a slow decrease in the pyrheliometric values, and presumably, therefore, in the solar constant; also during exactly this same interval the number of sun-spots slowly decreased. Again, from 1905 to 1911 the same general trends of the curves, a decrease in the pyrheliometric values simultaneously with a decrease in the number of sun-spots, repeat themselves. Hence the indication—it is impossible yet to call it a certainty—seems to be that the solar constant, and hence, presumably, the effective surface temperature of the sun, is a little, though not much, greater at the times of spot maxima than at the times of spot minima.



Relation of pyrheliometric values to sun-spot numbers and volcanic eruptions.

Surface Temperatures.—If a veil of dust actually should intercept as much as one-fifth of the direct solar radiation, as Fig. I indicates that at times it does, it would seem that in those years the surface temperatures of the atmosphere should be somewhat below the normal. Of course, the great supply of heat in the ocean would produce a lag in this effect, and, besides, there must be both an increase of sky light by scattering and some interception of earth radiation by the dust which, since it is at great altitudes, receives the full, or nearly the full, planetary radiation of the earth. This increase of sky radiation,

together with the return terrestrial radiation, obviously compensates in some measure for the loss of direct insolation.

However, measurements made by Abbot 27 at Bassour, Algeria, during the summer of 1912, show that at this time and place the direct radiation and the sky radiation, which obviously included both the scattered solar radiation and some return terrestrial radiation, were together less by about 10 per cent. than their normal combined values; and there is no reason to think that in this respect Bassour was at all different from other places, probably the whole earth, covered by the veil of dust. Clearly, then, if this decrease in the radiation received should continue indefinitely, the ultimate radiation of the earth would also decrease to the same extent, or 10 per cent. Now, since the earth, or rather the water vapor of the atmosphere, radiates substantially as a black body and therefore as the fourth power of its absolute temperature, it follows that a 10 per cent. change in its radiation would indicate about a 2.5 per cent. change in its temperature. But the effective temperature of the earth as a full radiator, which it closely approaches, is about 256° C.28 Hence a change of 10 per cent. in the radiation emitted would imply 6.4° C. change in temperature, an amount which, if long enough continued, would be more than sufficient to produce glaciation equal to the most extensive of any known ice age.

As above implied, not much lowering of the temperature could be expected to take place immediately, but, still, some cooling might well be anticipated. To test this point the temperature records of a number of high altitude (together with two or three very dry) inland stations have been examined. High altitudes were chosen because it might be expected that the temperature contrast between normal and dusty years would be greatest where the amount of atmosphere traversed below the dust layer is least; and the condition that the stations should also be inland was imposed because these are freer, presumably, than many coast stations, from fortuitous season changes. Thus, stations in the eastern portion of the United States are rejected because of the great differences in the winters, for example, of

<sup>&</sup>lt;sup>27</sup> Smithsonian Miscellaneous Collections, vol. 60, No. 29, 1913.

<sup>&</sup>lt;sup>28</sup> Abbot and Fowle, Annals Astrophys. Obsy., Smithsonian Institution, vol. 2, p. 175, 1908.

this section depending upon conditions wholly independent, so far as known, of variations in the intensity of direct radiation.

The number of stations was still further limited by the available recent data. Hence the records finally selected, and kindly put in shape by the Climatological Division of the United States Weather Bureau, Mr. P. C. Day in charge, for use in this article, were obtained at the following places:

TABLE I.
STATIONS WHOSE DATA WERE USED.

	America.		Florestica
Name.  Baker. Bismarck Cheyenne Denver. Dodge City El Paso Helena Huron. North Platte Red Bluff Sacramento Salt Lake City San Antonio Santa Fe Spokane Winnemucca Yuma	Latitude. 44° 46′ N. 46° 47′ N. 41° 08′ N. 39° 45′ N. 31° 45′ N. 46° 34′ N. 46° 34′ N. 41° 08′ N. 40° 10′ N. 38° 35′ N. 40° 46′ N. 29° 27′ N. 35° 41′ N. 47° 40′ N. 40° 58′ N. 40° 58′ N.	Longitude.  117° 50′ W. 100° 38′ W. 104° 48′ W. 105° 00′ W. 100° 00′ W. 106° 30′ W. 112° 04′ W. 98° 14′ W. 100° 45′ W. 122° 15′ W. 121° 30′ W. 111° 54′ W. 98° 28′ W. 105° 57′ W. 117° 25′ W. 117° 43′ W. 114° 36′ W.	Elevation in feet. 3,466 1,674 6,088 5,291 2,509 3,762 4,110 1,306 2,821 332 69 4,360 701 7,013 1,929 4,344 141
Mont Ventoux. Obir. Pic du Midi Puy de Dôme. Sāntis. Schneekoppe. Sonnblick	Europe.  44° 10′ N. 46° 30′ N. 42° 56′ N. 45° 46′ N. 47° 15′ N. 50° 44′ N. 47° 3′ N.	5° 16' E. 14° 29' E. 0° 8' E. 2° 57' E. 9° 20' E. 15° 44' E. 12° 57' E.	6,234 6,716 9,380 4,813 8,202 5,359
Simla	India. 31° 6′ N.	77° 12′ E.	7,232

In Table II the first column gives the year in question. The second column gives the average departure in degrees F., for the seventeen American stations, of the annual average maximum, as determined from the monthly average maxima, from the normal annual maximum, or average of a great many annual Vol. CLXXVI, No. 1052—12

average maxima. The third column gives smoothed values, determined from the actual values in the second column as follows:

$$S = \frac{a + 2b + c}{4},$$

in which S is the smoothed value, b the actual value pertaining to the particular year for which S is being computed, a and c the actual values for the next previous and the next succeeding years respectively. The fourth and fifth columns give respectively the actual and the smoothed average departures of the annual average minima, while the sixth and seventh columns give the corresponding average departures of the annual average means.

TABLE II.

Average Temperature Departures from Temperature Normals.

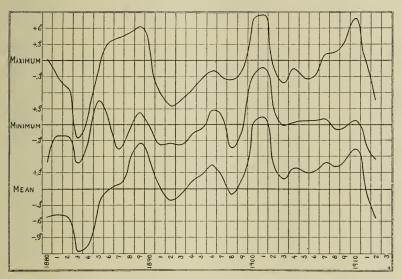
America.

		4	America.				
	Maxima.		Mir	Minima.		Means.	
Year.	Actual.	Smoothed.	Actual.	Smoothed.	Actual.	Smoothed.	
1880	-1.3	+0.03	<del>-</del> 1.8	-o.68	-I.7	-0.50	
1881	+0.2	-0.30	+0.6	-0.20	+o.1	-0.48	
1882	-0.3	-0.50	-0.2	-0.20	-0.4	-0.50	
1883	-1.6	-1.33	— I . O	-0.70	-1.3	-1.15	
1884	- I.8	- I . 20	-0.6	-0.28	<b>—</b> 1 . б	-1.05	
1885	+0.4	-o.18	+1.1	+0.43	+0.3	-0.30	
1886	+0.3	+0.35	+o.1	+0.10	-0.2	-0.03	
1887	+0.4	+0.38	-0.9	-0.45	0.0	+0.07	
1888	+0.4	+0.53	-o.i	-0.13	+0.5	+0.53	
1889	+0.9	+0.63	+0.6	+0.23	+1.1	+0.85	
1890	+0.3	+0.15	-0.2	-0.05	十0.7	+0.58	
1891	-0.9	-0.58	-0.4	<b>-</b> 0.38	-0.2	+0.05	
1892	-0.8	-0.85	-o.1	-0.33	-o.1	-0.20	
1893	-0.9	-0.73	-0.7	-o.38	-0.4	-o.o8	
1894	-o.3	-0.55	+0.4	-o.18	+0.6	+0.13	
1895	-0.7	-0.35	-0.8	-0.08	-0.3	+0.25	
1896	+0.3	-o.18	+0.9	+0.28	+1.0	+0.45	
1897	<b>-0</b> .6	-0.30	+0.I	+0.13	+o.1	+0.28	
1898	-0.3	-0.65	-0.6	-0.45	-o.1	-0.13	
1899	-o.8	-0.13	-0.7	-0.10	-0.4	+0.25	
1900	+1.4	+0.78	+1.6	+0.90	+1.9	+1.23	
1901	+1.1	+0.83	+1.1	+1.08	+1.5	+1.35	
1902	-0.3	-0.13	+0.5	+0.38	+0.5	+0.53	
1903	-1.0	-0.43	-0.6	-0.05	-0.4	+0.18	
1904	+0.6	-0.15	+0.5	+0.05	+1.0	+0.38	
1905	-0.8	-0.30	-0.2	+0.08	-o.1	+0.33	
1906	-0.2	-0.30	+0.2	+0.08	+0.5	+0.33	
1907	0.0	+0.10	+o.1	+0.10	+0.4	+0.50	
1908	+0.6	+0.15	0.0	-0.08	+0.7	+0.43	
1909	-0.6	+0.38	-0.4	-0.05	-o.ı	+0.55	
1910	+2.I	+0.80	+0.6	+0.08	+1.7	+0.75	
1911	-0.4	+0.03	-0.5	-0.35	-0.3	+0.05	
1912	-1.2	-0.70	-I.O	-0.63	-0.9	-0.53	

Fig. 3 shows the graphical equivalents of the smoothed portions of Table II.

It will be noticed that the three curves of Fig. 3, marked max., min., and mean respectively, are, in general, quite similar to each other. Hence, because of this mutual check and general agreement, we feel reasonably certain that any one set of tem-

Fig. 3.



Smoothed averages of the annual average temperature departures of 17 American stations.

perature data, the means for instance, furnishes a fairly safe guide to the actual temperature and climatic fluctuations from year to year or period to period.

Table III gives the weighted actual average departures and the smoothed departures in degrees F. of the annual mean temperatures of the selected seventeen American, seven European, and one Indian stations listed in Table I.

The average departures were calculated in accordance with the more or less correctly coefficiented equation,

$$D = \frac{4A + 2E + I}{7},$$

in which D is the weighted departure, A the smoothed average American, E the smoothed average European, and I the smoothed

Indian departure of the mean annual temperature from the normal annual temperature.

Table III, extended, as well as the scanty early data, mainly from the given stations, will permit, back to 1872, is graphically represented by the continuous light curve at the bottom of Fig. 4. In 1880 and again in 1901 the curve probably does not very

Weighted Departures of Mean Temperatures from Normal Temperatures.

World.					
Date.	Actual.	Smoothed.	Date.	Actual.	Smoothed.
1872	-o.78	-0.30	1893	-0.34	-0.06
1873	-o.65	-0.47	1894	十0.34	+0.03
1874	+0.20	-0.34	1895	-0.21	+0.10
1875	-I.I2	-0.61	1896	+0.49	+0.28
1876	-0.40	-0.60	1897	+0.34	+0.45
1877	<b>-</b> 0.48	-0.32	1898	+0.61	+0.46
1878	+0.07	0.00	1899	十0.27	+0.59
1879	十0.33	十0.04	1900	+1.19	+0.76
1880	-0.50	-0.13	1901	+0.40	+0.55
1881	+0.14	-0.02	1902	+0.20	+0.13
1882	+0.14	-0.16	1903	-0.30	+0.10
1883	-1.04	-0.68	1904	+0.81	+0.20
1884	-0.79	-0.61	1905	-0.51	+0.01
1885	+0.17	-0.09	1906	+0.23	+0.05
1886	+0.11	+0.03	1907	+0.23	+0.30
1887	-0.29	-0.05	1908	+0.51	+0.21
1888	+0.26	+0.24	1909	-0.43	+0.11
1889	+0.74	十0.57	1910	+0.69	+0.30
1890	+0.54	+0.40	1911	+0.23	+0.09
1891	-0.21	+0.06	1912	-0.80	-0.40
1892	+0.10	-0.09			

closely represent world-wide temperature departures, being, presumably, at both places quite too low, owing, in each case, to an abnormally cold single month in America.

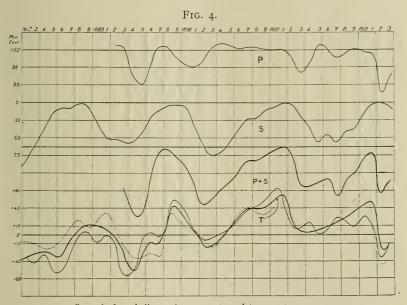
From 1907 to 1911 the dotted curve gives the average temperature departures for the American stations only, and presumably represents world temperature departures much more closely than does the continuous light line for the same time. This is because of two or three exceptionally cold summer months in Europe.

The dotted curve from 1872 to 1900 gives the smoothed averages of the annual temperature departures from the normal temperatures of the following stations as computed from the actual departures given by Nordmann: <sup>29</sup> Sierra Leone, Recife

<sup>&</sup>lt;sup>29</sup> Revue Général des Sciences, August, 1903, pp. 803-808. Annual Report, Smithsonian Institution, 1903, pp. 139-149.

(or Pernambuco), Port au Prince, Trinité, Jamaica, Habana, Manila, Hong Kong, Zikawei, Batavia, Bombay, Island of Rodriguez, Island of Mauritius.

All these, or practically all, are low-level stations, and most of them either tropical or semi-tropical, and therefore should show in general a smaller temperature range than the high altitude stations whose temperature departures are given by the continuous fine line curve. Hence, all things considered, the average temperature departures as calculated from the two sets



Smoothed pyrheliometric, sun-spot, and temperature curves.

of stations agree remarkably well, so that one can say with a fair degree of confidence that the heavy curve T approximately represents the average of the departures of the mean annual temperatures from the normal annual temperatures of the entire earth, or that T is the curve of world temperatures.

Relation of World Temperatures to Pyrheliometric Values.—Curve P, also of Fig. 4, gives the smoothed course of the annual average pyrheliometric readings, as computed from the actual values given in Fig. 1. The insolation intensity data, covering the whole of the depression that has its minimum in 1885, were

obtained at a single place, Montpellier, France, by a single observer, L. J. Eon,30 who confined himself to noon observations with a Croya actinometer. It may be, therefore, that merely local and temporary disturbances produced a local insolation curve that was not quite parallel to the curve for the entire world. At any rate, the drop in the solar radiation values obviously was due to dust put into the atmosphere by the explosion of Krakatoa in August, 1883, and it would seem that the effects of this dust both on the surface temperatures and on pyrheliometric values must have been greater during the latter part of 1883 and in 1884 than they were in 1885, when much of the dust certainly had already settled out of the atmosphere, and this supposition is well supported by the pyrheliometric and temperature drops that immediately followed the volcanic explosions of 1903 and 1912, and their partial recovery within a single year. Nevertheless, the pyrheliometric values must be accepted as obtained. Indeed, they appear to be somewhat supported by the fact that the coldest year following the similar. though more violent, explosion of Asamayama, just one hundred years earlier, was not the year of the explosion, 1783, nor the following year, but 1785.

It is probable that in the earlier, as certainly in the later, of these unusual cases the dust was thrown to such great altitudes that the finer portions were nearly, or quite, two years in reaching the lower level of the isothermal region. Clearly, too, much of this dust, while perfectly dry, probably was so fine as merely to scatter even solar radiation, and yet on reaching the humid portions of the atmosphere the particles may have gathered sufficient moisture to assume reflecting size, and therefore seriously to interfere with insolation. This is merely suggested, but in no wise insisted upon, as a possible explanation of the unusual pyrheliometric lag after the explosion of Krakatoa.

It is obvious, from a mere glance, that the pyrheliometric and the temperature curves, or curves P and T, have much in common. This is especially marked by the large and practically simultaneous drops in the two curves in 1912, following the eruption of Katmai. But while a relation between these curves thus appears certain, the agreement is so far from perfect as

<sup>&</sup>lt;sup>80</sup> Bulletin météorologique du Département de l'Herault, 1900.

to force the conclusion that pyrheliometric values constitute only one factor in the determination of average world temperatures.

Sun-spots and Temperature.—It has been known for a long time that the curve of sun-spot numbers, curve S, Fig. 4, and the curve of earth temperatures, curve T, follow or parallel each other in a general way, in the sense that the fewer the spots the higher the temperature, with, however, puzzling discrepancies here and there. Both these facts, the general agreement between the phenomena in question and also their specific discrepancies, are well shown by the curves S and T of Fig. 4, and, while the discrepancies are marked, it is obvious that, on the whole, the agreement is quite too close to leave any doubt of the reality of some sort of connection between sun-spots and atmospheric temperatures. Just how or by what process this relation exists will be discussed below.

Combined Effect of Insolation Intensity and Sun-spot Influence on Atmospheric Temperatures.—Since it is obvious that the insolation intensity and the number of sun-spots each exerts an influence on the temperature of the earth, it is clear that some sort of a combination of the two curves P and S should more closely parallel the temperature curve T than does either alone. It is probable that the sun-spot effect is not directly proportional to the actual number of spots, but, however this may be, the direct combination of the curves P and S gives the resultant P+S, which, as a glance at the figure shows, actually parallels the curve of temperatures T with remarkable fidelity. Exactly this same combination, from 1880 to 1909, has just been made by Abbot and Fowle,31 whose lead in this important particular is here being followed, and the resultant curve found to run closely parallel to the curve of "smoothed annual mean departures" of the maximum temperatures of fifteen stations in the United States.

Probably the most striking point of agreement, as shown by Fig. 4, between the combination curve and the temperature curve, occurs in 1912, where, in spite of the fact that the sunspots were at a minimum, the temperature curve dropped greatly and abruptly; obviously because of the simultaneous and cor-

sa Smithsonian Miscellaneous Collections, vol. 60, No. 29, 1913.

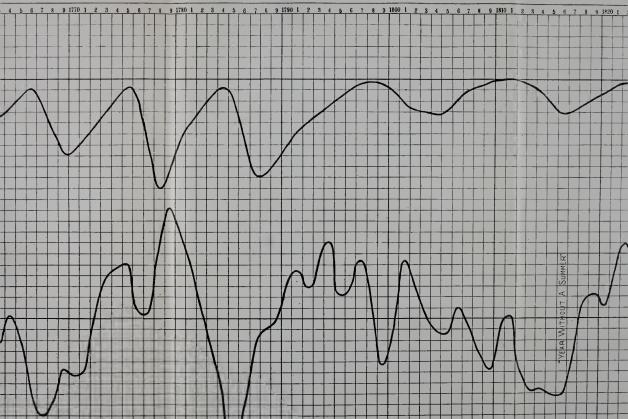
responding decrease in the intensity of solar radiation produced by the extensive (presumably world wide) veil of Katmai's dust.

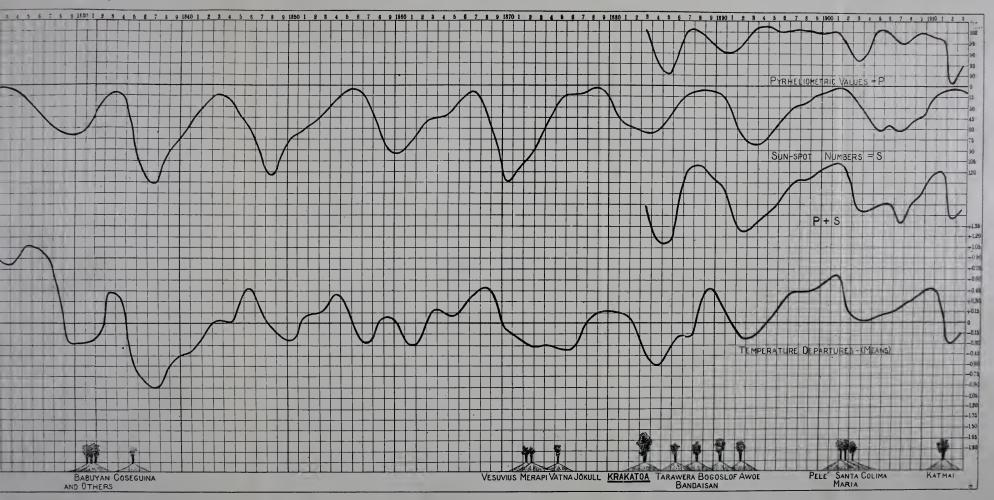
Temperature Variations Since 1750 as Influenced by Sunspots and Volcanic Eruptions.—Sun-spot numbers 32 month by month are fairly well known since July, 1749, and so, too, are the annual temperature variations 33 from about the same time, and therefore the data are at hand for comparing these two phenomena over a continuous period of a little more than 163 years, or from at least the beginning of the year 1750 to the present date. Fig. 5 makes this comparison easy. The bottom curve gives the smoothed annual temperature departures, as computed from Köppen's actual annual departures, using all stations, while the top curve follows Wolfer's annual average sun-spot numbers. Of course, the earlier observations, both of sun-spots and of temperatures, were few in number and more or less unsatisfactory in comparison with those obtained during the past thirty, or even forty, years. Nevertheless, it is clear from Fig. 5 that at least since 1750, the date of our earliest records, and presumably, therefore, since an indefinitely distant time in the past, the two phenomena, atmospheric temperature and sun-spot numbers, have in general varied together, with, however, marked discrepancies from time to time. These we shall now consider, and show that they occurred, in every important case, simultaneously with violent volcanic eruptions.

Volcanic Disturbances of Atmospheric Temperature Since 1750.—It must be distinctly remembered that the earlier temperature records, because of their limited number, if for no other reason, can give us only the general trend of world temperatures. Again, the record back to 1750 of even violent volcanic eruptions is necessarily incomplete; and, besides, not all great eruptions decrease the world's temperature—only those that drive a lot of dust into the isothermal region. Extensive and long-continued sky phenomena, therefore, of the type that followed the eruption of Krakatoa, furnish the best evidence of volcanic violence in the sense here used. Finally, there can be no particular test save where the temperature is low in com-

<sup>&</sup>lt;sup>82</sup> Wolfer, Astronomische Mitteilungen, 93, 1902, and later numbers.

<sup>&</sup>lt;sup>33</sup> Köppen, Zeit. Österreich. Gesell. für Meterologie, vol. 8, 241 and 257, 1873.





parison with that which the number of sun-spots would lead us to expect. Obviously, then, no matter how close the actual relation between the phenomena may be, the errors and the incompleteness of the recorded data would prevent the discovery of more than a general relation.

Of course, it will naturally occur to one to ask about special cases, such as the cold years of 1783–4–5, and, in particular, 1816, the famous "year without a summer," "poverty year," or "eighteen hundred and froze to death." The first of these, 1783–5, followed, as already explained, the great explosion of Asama in 1783, while the second, the "year without a summer," that was cold the world over, followed the eruption of Tomboro, which was so violent that 56,000 people were killed 34 and "for three days there was darkness at a distance of 300 miles." 35

There is a detail in the temperature curve for the years 1886–7 that needs special attention. The temporary depression where, seemingly, the temperature should be steadily rising, obviously was due to the great eruption of Tarawera, in New Zealand. This volcano is a little more than 38° south of the equator, and therefore furnishes a good example of an eruption on one side of the equator affecting the temperature far to the other side. Doubtless, however, when the dust gets but a little way into the isothermal region the effect is greatest on the volcano's side of the equator.

But if the temperature was decreased by Tarawera, why, one might ask, was not the pyrheliometric curve similarly affected? It was, for several months after the eruption, as the individual monthly values show, but the annual means, plotted in the figure, have the effect of making the pyrheliometric disturbance from Tarawera appear only as a retardation in the recovery from Krakatoa.

Neglecting the smaller irregularities which may or may not have been of world-wide occurrence, and remembering that, other things being equal, we may expect temperature maxima at the times of spot minima and temperature minima at the times of spot minima, we can tabulate as follows the marked discrepancies and their probable explanations:

<sup>&</sup>lt;sup>34</sup> Schneider, Die Vulcanischen Erscheinungen der Erde, p. 1, 1911. <sup>25</sup> Rept. Krakatoa Committee Royal Society, 1888, p. 393.

## TEMPERATURE AND SUN-SPOT DISCREPANCIES.

Nature	
Date discrepan	
1755–6 Cold.	Kötlugia, Iceland, 1755.
1766-7 Cold.	Hecla, Iceland, 1766.
	Mayon, Luzon, 1766.
1778–9 Warm	. Maximum number (annual) of sun-spots ever recorded
	and unusually short spot period. Can it be that
	the solar constant actually was distinctly greater
	than usual at this time?
1784-5-6 Cold.	ASAMA,* Japan, 1783. The most frightful eruption
	on record.
	Skaptar Jökull, Iceland, 1783.
	Vesuvius, Italy, 1785.
1700 Cold.	Fuego (?), Guatemala. (Uncertain.)
1800 Cold.	St. George (?), Azores, 1808. (Uncertain.)
200911111111111111111111111111111111111	Etna (?), Sicily, 1809. (Uncertain.)
1812-13-14-15-16. Cold.	Soufrière, St. Vincent, 1812.
1012 13 14 13 10. 0010.	Mayon, Luzon, 1814.
	TOMBORO, Sumbawa, 1815, very great.
1831-2 Cold.	
1031 2	Babujan Islands, 1831
	Pichincha, Ecuador, 1831.
1856-7 Cold.	Cotopaxi (?), and others, 1855-6. (Uncertain.)
1872-3 Cold.	Vesuvius, Italy, 1872.
10/2 3 00141	Merapi, Java, 1872.
1875-6 Cold.	Vatna Jökull, Iceland, 1875.
1884-5-6 Cold.	KRAKATOA, Straits of Sunda, 1883, greatest since
1004 3 077777777 00101	1783.
	Saint Augustin, Alaska, 1883.
	Tarawera, New Zealand, 1886.
1800-1-2 Cold.	Bogoslof, Aleutian Islands, 1890.
1090 1 211111111111111111111111111111111	Awoe, Great Sangir, 1892.
1902-3-4 Cold.	
1902 3 4	Santâ Maria, Guatemala, 1902.
	Colima, Mexico, 1903.
1912-13 Cold.	

<sup>\*</sup> This type indicates exceptional violence.

The above list does not dispose of all the seeming irregularities, nor of all the known volcanic eruptions; but it does dispose of all the well-defined and unquestioned irregularities and also of every one of the known really great volcanic explosions since 1750.

We may conclude, therefore, that the variations in the average temperature of the atmosphere depend jointly upon volcanic eruptions, through the action of dust on radiation, as already explained, and upon sun-spot numbers, through, presumably, some intermediate action they have upon the atmosphere—possibly of the nature we shall now explain.

How Sun-spots May Change Earth Temperatures.—If the solar constant remains the same from spot maximum to spot min-

imum it clearly is not easy to see at a glance why the surface temperature of the earth should vary as it does with spot numbers; and the situation is still more difficult if, as observations appear to indicate, our lowest temperatures occur when the solar constant is greatest and our highest temperatures when this constant is least! There is, however, a possible explanation of the paradox, and, while it may not contain the whole truth, it nevertheless is sufficient to show a priori that in all probability our temperatures do change from spot maxima to spot minima without a corresponding change in the solar constant, and also to show that a decrease in our surface temperatures may accompany even a slight increase in the solar constant.

The explanation in question has already been given elsewhere,<sup>36</sup> and the original paper must be consulted by those who wish to weigh all the details of the argument. Briefly, how-

ever, the argument is as follows:

I. At the times of spot maxima the solar corona is much more extensive than it is at the times of spot minima—a well-known observation.

- 2. This corona consists, in part at least, of reflecting particles, as many eclipse observations have shown, and so may be regarded as dust in the solar atmosphere.
- 3. The brightness of the sun, as every solar observer knows, drops off from centre to limb.
- 4. This drop, as reported by various observers, is greater the shorter the wave-length, and due, almost certainly, to diffuse scattering.

From the observational facts it follows that during spot minima, other things being equal, the solar spectrum must necessarily be richer in violet and ultra-violet radiation than it is during spot maxima.

But, as experiment has shown,<sup>37</sup> ultra-violet radiation of shorter wave-length than  $\lambda$  1850 is strongly absorbed by oxygen, with the result that some of the oxygen is converted into ozone. Hence since the atmosphere of the isothermal region is cold and dry (conditions favorable to the stability of ozone), and since of the gases of the upper atmosphere only oxygen is appreciably

<sup>38</sup> Humphreys, Astrophys. Ir., 32, p. 97, 1910.

<sup>37</sup> Lyman, Astrophys. Jr., 27, p. 87, 1908.

absorptive of radiations between  $\lambda$  1250 and  $\lambda$  1900,<sup>38</sup> we should confidently expect it to contain more or less ozone, an expectation greatly strengthened by the observations of Fabry and Buisson,<sup>39</sup> though already virtually confirmed by Ångström.<sup>40</sup> In so far then as this ozone is produced by the action of ultraviolet solar radiation, we should also very definitely expect it to be greater in quantity when the short wave-length radiation to which it is due is most intense, or, presumably, therefore, at the times of spot minima. Now, according to the experiments of Ladenburg and Lehmann,<sup>41</sup> while ozone is somewhat absorptive of solar radiation it is several-fold more absorptive, in fact highly absorptive, of terrestrial radiation. Hence in this case, as in the case of the absorption of radiation by dust, already considered, equation A, page 139, is applicable.

In this equation let a be the coefficient of absorption of the ozone in the isothermal region for solar radiation, and b its coefficient of absorption for earth radiation. To be definite, let a=0.02 and b=0.10 at the time of a spot maximum, and for a spot minimum let a=0.03 and b=0.15, quantities that would require really very little ozone. Then, remembering that the earth radiates practically as a full radiator, or black body, at the absolute temperature  $256^{\circ}$  C., and taking  $T_{\rm max}$  and  $T_{\rm min}$  as the equilibrium temperatures at the time of spot maximum and spot minimum respectively, we get

$$\left(\frac{T_{\text{max.}}}{256}\right)^4 = \frac{521}{500}; T_{\text{max.}} = 258^{\circ}.65.$$

and

$$\left(\frac{T_{\text{min.}}}{256}\right)^4 = \frac{2129}{2000}; T_{\text{min.}} = 260^{\circ}.05.$$

That is, under these conditions, and if the solar constant should remain exactly the same, the temperature at the time of spot minimum would be 1°.4 °C. warmer than at the time of spot maximum. Hence, even a slight increase in the solar constant at the time of spot maximum might still leave the temperature a trifle cooler than at the time of spot minimum.

<sup>28</sup> Lyman (l. c.).

<sup>30</sup> C. R., 156, p. 782, 1913; Journal de Physique, 3, p. 196, 1913.

<sup>40</sup> Arkiv för Matematik, Astronomi och Fysik, 1, p. 395, 1904.

<sup>&</sup>lt;sup>41</sup> Annalen der Physik, 21, p. 305, 1906.

Of course, it is not claimed that the above gives, both quantitatively and qualitatively, exactly what happens, but it is claimed that it does show qualitatively what might happen, and, so far as we can judge from observations and laboratory experiments, what actually must happen.

Influence of Carbon Dioxide on Temperatures.—It was stated in the early part of this paper, under the carbon dioxide theory of ice ages, that the question of the possible effect a change in the amount of carbon dioxide in the atmosphere might have on temperatures would be taken up later. The way to this is now open through the above discussion of ozone. Like ozone, carbon dioxide also is more absorptive of terrestrial radiation than of solar energy. Hence increasing the carbon dioxide in the atmosphere, and thereby increasing its amount in the isothermal region where we can treat it as a shell external to the radiating earth. obviously must have the same general effect on the temperature of the earth as increasing the ozone of this region would have. That is, other things being equal, a greater or less temperature increase would follow the introduction into the atmosphere of a larger amount of carbon dioxide.

Because of the constant mixing caused by vertical convection it is probable that the percentage of carbon dioxide is very nearly as great at the under surface of the isothermal region as it is at the surface of the earth. If so, then the carbon dioxide of the isothermal region is equivalent, roughly, to a layer 40 centimetres thick at normal atmospheric pressure. In high latitudes, where the isothermal level is low, the equivalent layer probably is thicker than this, and in equatorial regions probably thinner. Now, according to the experiments of Schlaefer, <sup>42</sup> a layer of carbon dioxide 40 centimetres thick is sufficient to produce very nearly full absorption, and therefore no increase in the amount of carbon dioxide in the atmosphere could very much increase its temperature.

An approximate idea of the possible temperature change of the lower atmosphere as a result of the presence of carbon dioxide in the isothermal region can be obtained from known data. Thus Abbot and Fowle 43 have computed that carbon dioxide

<sup>&</sup>lt;sup>42</sup> Ann. der Physik, 16, p. 93, 1905.

<sup>43</sup> Annals Astrophys. Obsy., Smithsonian Inst., vol. 2, p. 172, 1908.

may absorb 14 per cent. of the radiation from a black body at the temperature of 282.2° C. absolute. But as this is not many degrees, 25 or so, above the effective temperature of the earth as a radiator, it follows that 14 per cent. is, roughly, the upper limit to which terrestrial radiation can be absorbed by carbon dioxide in the isothermal region, while its absorption of solar radiation is very nearly negligible.

Assuming that the present amount of carbon dioxide in the isothermal region absorbs 1 per cent. of the solar radiation and 10 per cent. of the outgoing earth radiation (values that seem to be roughly of the correct order), and using equation A as above, it will be seen, if the experiments here referred to and the assumptions are substantially correct, that doubling or even multiplying by several-fold the present amount of carbon dioxide could increase the average temperature by no more than about  $1.3^{\circ}$  C. Similarly, reducing the carbon dioxide by one-half could decrease the temperature by no more than approximately the same amount,  $1.3^{\circ}$  C.

It is not certain to what extent the percentage of carbon dioxide in the atmosphere has actually varied during the geological past, but, if the above reasoning is correct, it seems that our surface temperatures could never have been much increased above their present values through the action of this particular agent alone. Further, the fact, so far as known, that within the tropics, at least, plant growth, even during the ice ages, was quite as vigorous during the past as it is at present, shows that for many ages carbon dioxide has been abundant in the atmosphere—probably never much less abundant than at present. Hence it seems likely that a decrease in temperature of a fraction of one degree is all that can reasonably be accounted for in this way.

Finally, if the above reasoning is correct, it seems that changes in the amount of carbon dioxide in the atmosphere might have been a factor in the production of certain climatic changes of the past, but that it could not, of itself, have produced the ice ages.

Having considered, in the above long digressions, the observational evidence of temperature changes in connection with volcanic explosions, we are ready again to take up the main sub-

ject and to consider one or two more of the physical problems it

presents.

Number of Dust Particles.—The intensity of the solar radiation  $I_x$  after it has passed through x centimetres of the dust layer of the atmosphere is given, as we have seen, by the equation

$$I_x = Ie^{-2n\pi x} (92)^2 \times 10^{-12}$$

But, according to numerous observations made during the summer and fall of 1912, when the solar radiation had passed entirely through the dust layer at such an angle that it met, roughly, twice as many dust particles as it would have met had it come in normally, or from the zenith, it was reduced by about 20 per cent. That is to say, under these conditions

$$I_x = 0.8 I.$$

Hence

$$10 = 8e^{2nx\pi} (92)^2 10^{-12}$$

Let nx = 2N, the total number of particles passed in a cylinder of one square centimetre cross section. Then

$$10 = 8e^{4N\pi} (92)^2 10^{-12}$$

Hence the number of particles in a vertical cylinder of one square centimetre cross section is given, roughly, by the equation

$$N = 34 \times 10^4$$
.

Temperature Correction Due to Dust Radiation.—With the number and size of the dust particles we are in position to determine at least an upper limit to the effect of the direct radiation of the particles themselves on the temperature of the earth.

The temperature of the dust particles, obviously, is very nearly that of the upper atmosphere in which they float and therefore, as we have seen, approximately — 55° C., or 218° C. absolute. As we have also seen, the quantity of radiation from the atmosphere below the isothermal region is substantially that which would be given off by a full radiator at 256° C. absolute.

Now assume the dust particles to be concentrated side by side on a common plane, and further assume them to be full

radiators—conditions that would raise their effect to the theoretical upper limit. Let E be the intensity or quantity per square centimetre of the outgoing planetary radiation, and D the intensity of the incoming dust radiation. Then

$$E: D = (256)^4: a (218)^4,$$

in which a is the projected area of all the particles in a vertical cylinder of one square centimetre cross section.

But

$$a = 34 \times 10^4 (92)^2 10^{-12} = 9 \times 10^{-3}$$

Hence

$$E = 211 D.$$

Now when the radiation D is absorbed by the lower atmosphere it follows that its temperature will be so increased that, when equilibrium is reached, the intensity of its new radiation will be to that of its old as 212 is to 211. Hence  $\Delta T$ , the effective temperature increase of the lower atmosphere, is given by the equation

$$\frac{(256 + \triangle T)^4}{(256)^4} = \frac{212}{211},$$

from which

$$\triangle T = 0^{\circ}.3 \text{ C}.$$

But, as stated above, the dust particles, presumably, are not full radiators, and therefore probably one-fifth of a degree C. is as great an increase in temperature as may reasonably be expected from this source. But this *increase*, 0.2° C., is small in comparison with the *decrease*, 6° C. to 7° C., caused by the interception of solar radiation, already explained. Hence it appears reasonably certain that the sum total of all the temperature effects produced by volcanic dust in the upper atmosphere must be, if long continued, a lowering of the surface temperature by several degrees C.

Total Quantity of Dust.—Let nx = 2N, the total number of particles passed in a cylinder of one square centimetre cross section. Then

$$10 = 8e^{4N\pi (92)^2} \times 10^{-12}$$

Hence

 ${\it N}=34\times 10^4\,{\rm roughly}={\rm number}$  of particles in a vertical cylinder of one square centimetre cross section.

If A is the entire area of the earth in square centimetres, then the total number of dust particles is

$$NA = 1734 \times 10^{21}$$
.

But the radius of each particle is  $92 \times 10^{-6}$  cm., and its volume, assuming it spherical,  $33 \times 10^{-13}$  cubic centimetres. Hence the total volume of the dust, assuming the particles spherical, is equal, roughly, to a cube 179 metres, or about 587 feet on the side, an amount that certainly is not prohibitively large.

As just stated, the total quantity of dust sufficient, as we have seen, to cut down the intensity of the direct solar radiation by 20 per cent., and therefore, if indefinitely continued, capable, presumably, of producing an ice age, is astonishingly small,—only the 174th part of a cubic kilometre, or the 727th part of a cubic mile, even assuming that the particles are spherical. Since, however, in large measure, the particles are more or less flat, as already explained, it follows that the actual total mass of the dust necessary and sufficient to reduce the intensity of direct solar radiation by 20 per cent. probably is not more than the 1500th part of a cubic mile, or the 350th part of a cubic kilometre.

Hence, even this small amount of solid material distributed once a year, or even once in two years, through the upper atmosphere, would be more than sufficient to maintain continuously, or nearly so, the low temperature requisite to the production of an ice age; nor would it make any great difference where the volcanoes productive of the dust might be situated, since, from whatever point of introduction, the winds of the upper atmosphere would soon spread it more or less evenly over the entire earth.

A little calculation will show, too, that this quantity of dust yearly, during a period of 100,000 years, would produce a layer over the earth only about half a millimetre, or one-fiftieth of an inch, thick, and therefore one could hardly expect to find any marked accumulation of it, even if it had filled the atmosphere for much longer periods.

Inherent Ability of the Earth to Produce its Own Climatic Changes.—Whether periods of explosive volcanic activity—and in this case, since the locality of the volcano is a matter of small importance, the whole earth must be considered—occurred at such times as to synchronize with the ice ages and with other Vol. CLXXVI, No. 1052—13

epochs of great climatic change is, of course, a problem for the May it be that extensive upheavals and geologist to solve. great volcanic activity were synchronous? If so, their climatic effects must have been additive. Increase in land elevation would, because of the resulting decrease in temperature, extend the area of snow and ice, and the snow, in turn, through its power to reflect sunlight, would decrease the amount of solar energy actually absorbed, and thus still further extend the ice sheet, and so on through an indefinite though decreasing and limited series. Besides, an elevation of any considerable extent is pretty certain to be accompanied by increase in continental area and radical modification of shore lines, such that greater or less changes would follow in the direction, temperature, and magnitude of ocean currents, location, number, and intensity of the permanent "highs" and permanent "lows," direction and force of local winds, amount of local precipitation, and a host of other meteorological phenomena. Thus, as the oceans and continents are now related to each other the main drift of warm water from the tropics is toward the north and not toward the south, but a change in the relation of land and water that would reverse this proportion obviously would have the result of leaving the northern hemisphere, especially in higher latitudes, perceptibly colder than it now is, and of producing many other climatic changes, all of which it would be interesting to discuss from the standpoint of modern meteorology, though that would be beyond the restricted purpose of this paper—a consideration of the climatic effects of volcanic dust.

It is surmised, therefore, that the greatest of our past climatic changes may have been caused by the combined and, roughly, simultaneous variations in continental level and volcanic activity; cold periods coming with increase in elevation and increase in vulcanism, minor climatic oscillations with temporary changes in vulcanism, and warm periods when the land had gone back to low levels and volcanoes had ceased greatly to veil the skies with dust. But while great changes in level, such as probaby have several times occurred, and great changes in vulcanism, such as also have occurred, would, even separately, produce climatic changes, it remains for the geologist to determine just what was the relation of these phenomena to each other and to the great climatic changes with which he is so deeply concerned.

However, this much appears well-nigh certain: Since the beginning of reliable records, say 160 years ago, the average temperature of the earth has been perceptibly lower, possibly as much as 1° F., than it would have been if during all this time there had been no volcanic explosions violent enough to put dust into the isothermal region of the atmosphere. Similarly, on the other hand, if, during this period, violent volcanic explosions had been three or four times more numerous than they actually were, our average temperatures probably would have been at least 2° F. to 3° F. lower, or low enough, if long continued, to bring on at least a moderate ice age.

As already stated, it may be that our great climatic changes have been caused by corresponding changes in the output of solar energy, though at present this seems wholly impossible either definitely to prove or clearly to disprove; but, however they actually were produced, it is probable, if not entirely certain, that, given an invariable or nearly invariable solar constant, the earth itself possesses potentially the power of bringing about its own climatic changes—even of beginning and of ending its own ice ages, and its own periods of genial climates.

Magnitude and Importance of Actual Temperature Changes.—The actual temperature range from sun-spot maximum to sunspot minimum varies, roughly, from 1° F. to 2° F., or possibly more, while the effect of volcanic dust appears to be fully as great—on rare occasions even much greater. In some ways, and in respect to many things, a range of average temperatures of 2° F. is well-nigh negligible, and therefore, however important the results may seem to the scientist, the ultra utilitarian would be justified in asking, "What of it?"

Much of it, in a distinctly practical as well as in a purely scientific sense, as is true of every fact of Nature. For instance, during the summer or growing season a change of 1° F. produces a latitude shift of the isotherms by fully 80 miles. Hence, if there is but little or no volcanic dust to interfere, during sunspot minima cereals and other crops may successfully be grown 50 to 150 miles further north (or south in the southern hemisphere) than at the times of sun-spot maxima. This alone is of great practical importance, especially to those who live near the thermal limits of crop production.

In addition to changing the area over which crop production is possible, a change of average temperature also affects, in some cases greatly, the time of plant development. Thus Walter 44 has shown that a change of only 1.26° F. may alter, and in Mauritius has been observed actually to alter by as much as an entire year, the time required for the maturing of sugar cane. Hence the temperature changes that normally accompany sun-spot variations, though small in absolute magnitude, are of great importance, and, by availing ourselves of the reasonable foreknowledge we have of these changes, may easily be made of still greater importance.

In forecasting these small but important climatic changes it must be distinctly remembered that to the fairly periodic and therefore predictable, sun-spot influence must be added the irregular and unpredictable volcanic effects. But even here the case is not bad for the forecaster, since the volcanic dust always produces, qualitatively, the same effect—a cooling—and since both the amount of this cooling and its duration may approximately be estimated from the nature of the volcanic explosion itself.

## CONCLUSION.

It has been shown in the above, among many other things, that volcanic dust in the high atmosphere decreases the intensity of solar radiation in the lower atmosphere, and therefore the average temperature of the earth, substantially as theory indicates a priori that it should; and this effect has been clearly traced back to 1750, or to the time of the earliest reliable records. Hence it is safe to say that such a relation between volcanic dust in the upper atmosphere and average temperatures of the lower atmosphere always has obtained, and therefore that volcanic dust must have been a factor, possibly a very important one, in the production of many, perhaps all, past climatic changes, and that through it, at least in part, the world is yet to know many another climatic change in an irregular but well-nigh endless series—usually slight, though always important, but occasionally it may be, as in the past, both profound and disastrous.

<sup>&</sup>lt;sup>44</sup> On the Influence of Forests on Rainfall and the Probable Effect of "Déboisement" on Agriculture in Mauritius (1908).

## THE ELECTRICAL EQUIPMENT OF A MODERN BATTLESHIP.<sup>1</sup>

BY

### H. A. HORNOR, B.A.,

Member of the Institute.

One of the reasons underlying the appropriation of large sums of money by civilized nations each year for the construction of ships of the line is an endeavor to define and produce the modern battleship. Time in which to execute this work, and the development of the arts and sciences, act to defeat this purpose. A period of about four years is required to prepare the design and construct the vessel; and during this time only small changes in equipment can be made.

Although the electric plant of a battleship is a small part of the whole equipment, yet, like the nerves of the human body, it comes in contact with every part. As the work of installation requires about one year, and obviously cannot be commenced until the structure of the vessel is prepared for its reception, it is possible to give careful consideration to details. So rapid, however, are the improvements in the art and practice of electricity that the latest commissioned battleship hardly satisfies the term modern.

The substance of this paper, therefore, will be suggestive rather than historical. The intention is to suggest certain modifications to the present equipment, based on land usages and their adaptation for marine purposes. This will occasion reference to the practice of many nations, and will, so far as the writer knows, set forth an electrical equipment installed at the present time by none.

## GENERATION OF ELECTRICITY FOR LIGHTING AND AUXILIARY POWER,

On the question of the centralization, or the distribution of the generating sets, opinions differ. To put all your eggs in one basket when you are going into battle would appear to favor separation or distribution, but it would seem ridiculous to value the electric plant above that of the propelling machinery.

<sup>&</sup>lt;sup>1</sup> Presented at the joint meeting of the Electrical Section and the Philadelphia Section, American Institute of Electrical Engineers, held Thursday, April 3, 1913.

Though separated by a bulkhead, the main engines are practically in one compartment, protected under water by cellular water-tight compartments. An under-water attack might cripple these engines and so disturb the steam conditions that the electric plant, though preserved, would be of little value. It may be said, on the contrary, so long as you have electricity and can operate your guns with this power, just so long you may fight.

In the future there will be developed a generating unit which is not dependent upon the same source of power as the propelling machinery. Then a small unit may be installed in each turret in order that the turret may, in a sense, become a self-contained fortress. This would provide the very best strength for the

man-of-war.

There is only one more matter for consideration in this discussion, and that a curious one. On land we are comparatively free in the paralleling of generators, and think little of "throwing in" another generator into the general network of the distributing system; but on war vessels the complications for effecting such operations do not seem to please, and in many cases positive preventative measures are taken to avoid its possible occurrence. Like most of the applications of electricity, it has not been without trial, and the performance, from all reports, was satisfactory.

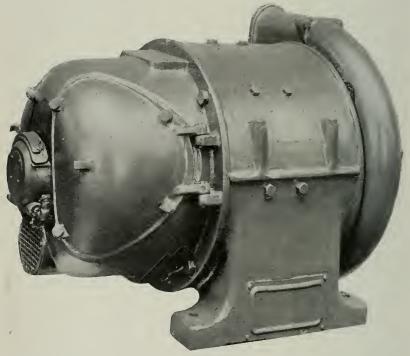
Given the sum of your lighting, battle, and power load, and the total kilowatt capacity is settled. Then arises the question of size of unit. The largest unit, to the author's knowledge, now furnished is 375 kilowatts. With units of this size a fairly economical arrangement for ordinary day and night loads, with a safe battle reserve, can be worked out. It is most desirable to provide a spare unit for battle conditions, for no one can conceive of the possible exigencies of war. If the electric plant of war vessels has doubled in the last decade we may well expect a like increase in the future. As the development of auxiliary apparatus continues so will the daily load be added to, and it may be expected that very shortly 500-kilowatt generators will be placed in service.<sup>2</sup>

<sup>&</sup>lt;sup>2</sup> Some European powers install small oil engine-driven generators for use when the vessel is in harbor. This permits the drawing of the fires, allowing the boilers to be cleaned and repaired. This outfit is of such size, approximately 150 kilowatts, that not only the ordinary loads but also the gun practice loads may be carried.

Direct current is universally employed, due to the early development of suitable apparatus and because we are all so familiar with it. It is reported vaguely that some European nation has made trial of a mixed alternating current-direct current system on some small craft, but definite results of such an equipment are not available. Our British brothers, with a 3-wire system, use 110 volts for lighting, and operate their motors on 220 volts from the outer wires. In this country we stepped up and down in voltage about eleven years ago. In 1899 the Kearsarge and Kentucky were wired for 80 and 160 volts. In 1902 our Government adopted, in accordance with the standardization rules of the A. I. E. E., a voltage of 125. Our Japanese friends hold to a voltage of 50. In contrast, we find the new Argentine battleships provided with 220 volts on a straight 2-wire system. This choice of voltage is based on the development of the incandescent lamp. The lighting system for this period has been the sole consideration for the use of electricity. The increased use of electric motors has now changed the problem almost to the extent of making the lighting system of secondary importance.

This ever-increasing motor load must be the subject of thought to-day; and with it comes the necessity for economy in fuel consumption and reduction in weight. Even in our present steam-propelled vessels the use of electricity for the economical operation of auxiliaries presents a large field. It was only a few years ago that this modern power entered the domain of the steam engineer in the form of forced-draft fans; but this was quite sufficient to convince him of the benefits well present in the mind of the electrical engineer. Electricity is ready to furnish power for air-pumps, water circulating pumps, and eventually that difficult application—boiler-feed pumps. In the deck department already such applications as the anchor windlass and steering gear have been made, and we can expect that with these fully accomplished further applications will present themselves. With this problem before us, and the question of transmission set aside for the present, would it be reasonable to consider the use of alternating current instead of direct current? There is no doubt that an increase of voltage with direct current will help conditions; but it will not completely solve the problem or give that flexibility for expansion that alternating current inherently possesses. Of course, a hasty jump to a higher voltage

would doubtless frighten all parties interested, but we are referring to not a low potential but an insignificant one from the viewpoint of present land practice. There would be little gained by using 125 volts direct current; but why should not the alternating current voltage be taken very much higher? Our knowledge of insulation and the manufacture of insulating



Type of totally enclosed, ventilated, splash-proof, split-frame motor used in connection with pumps for flushing purposes. This is a special design prepared to reduce the size of motor and retain the necessary horsepower. Rated capacity of motor, 35 horsepower, 1200 revolutions per minute, 220 volts.

materials has followed the developments of land practice, and the writer believes that we are able to cope with this question aboard ship.

Control of generating sets aboard ship is not difficult, and there seems some uniformity with remote control coming into its share of consideration. This latter operation should be entirely automatic and fool-proof. It is unquestionable that the automatic operation of switches, circuit breakers, rheostats, etc., has gained such a reliable place in the opinion of land engineers that the application of this apparatus to shipboard is entirely reasonable. Provided with pilot lights and mechanical signals, a bench board as installed in many of our large central stations would be an engineering advance and also of importance from a military point of view, where the elements of time and order are principal factors.

#### AUXILIARIES.

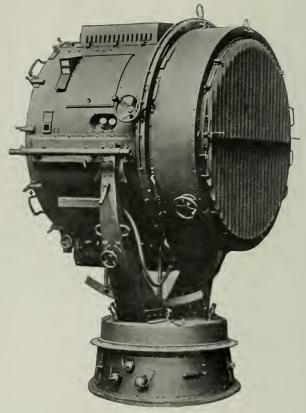
The lighting of a vessel is really an auxiliary, and should have due consideration, although now passing into second place compared to power. There is a growing confidence in the wiredrawn tungsten lamp for all lighting purposes, superseding the arc lamp for large spaces and coaling ship—this latter, of course, not being essential to an oil-burning vessel. Carbon filament lamps may still preserve their usefulness in and about compartments where machinery causes severe vibration. It speaks well of the manufacture of tungsten lamps when their reliability is so highly valued that all spring-type lamp sockets are being rapidly replaced by the ordinary commercial type. This practice is now adopted by nearly all nations. Large single unit lamps are used for boiler rooms, engine rooms, and gangway lamps.

Searchlights still hold an important place in this installation, and the practice of each nation seems to oscillate between a large number of fair size, say 30- or 40-inch, and a small number of large size, say 60-inch. Experiments are now proceeding in England on the deposition of gold to produce an effective mirror instead of silver. The former has many points in its favor: it is not affected by chemical or climatic conditions, more effective in foggy weather, due to large percentage of red and yellow rays, absence of halos, and is an easier light for distinguishing shades of gray.

For convenience, electric heating is classified as power, due, no doubt, to its present modest application. It is foreseen that it will in time achieve a more distinctive place in the equipment. At present electric ranges, bake-ovens, and radiators are installed and are giving good return for their introduction. They furnish a heavy part of the cruising load, and probably will be a reason for increasing the size of generating units. This application is

so young that there can be no positive statement made, yet the rapid improvements already seen give promise of greater applications in the future.

Approximately 100 kilowatts maintain the lighting system, and the balance of the 1500 kilowatts is then available for power



Electrically-controlled searchlight, permitting operation at a distance. The signalling shutter may also be automatically operated at a remote point.

purposes. This is divided roughly into auxiliaries that are used only when cruising, or at anchor, or in port: those used in battle only; and those which lap over and are used in both cases. To go backwards, the steering gear would be used while in battle as well as when cruising; the turret machinery would be used only in battle; and the anchor or windlass would be used

only when about to weigh anchor. The problems of design for all these auxiliaries are extremely interesting not only to the electrical engineer from the electrical features, but also because of the military questions involved. These auxiliaries have a great bearing on the above suggested change from direct current to alternating current. The question of speed control arises, but, as a matter of fact, it is of little moment. Every application of a direct-current motor could be just as readily met with the alternating-current motor; and for the most part with the squir-



Type of totally enclosed, water-tight, direct-current motor. Note water-tight box arranged for protecting the terminals and providing proper facilities for entering feeders.

rel-cage induction motor. Where great variations of speed are needed they will be found in some minor application, not in the significant ones. A marked improvement recently is the increasing use of contactor control, which enables the vital parts of the control to be placed below the weather deck where it can be easily cared for and will not be endangered when the vessel is subjected to the enemy's fire. This feature of remote control gives an added weight and importance to the electric motor application, which is seen in its sharpest outline by the revival of the electric steering gear. It is expensive to lead piping all over a vessel, but

there is no hardship attached to the running of a comparatively small cable. It is then possible to steer the vessel in many

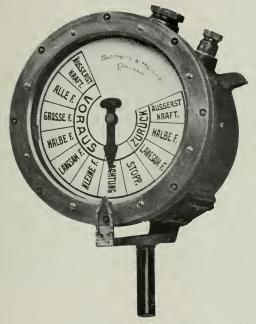


Electric engine telegraph transmitters for communication between the bridge and the engine room. The three transmitters connect separately to receivers located in their respective engine rooms. Instruments are arranged for reply signal.

places; and in the case of emergency the transfer from one place to another can be made in a very small fraction of time.

The signalling system is another important and extensive

auxiliary on a modern man-of-war. It now very nearly equals in cost the power and lighting systems. Following the service it performs, it is divided into many subdivisions, comprising telephones, telegraphs, call-bells, voice-tubes, control of gunfire, etc.<sup>3</sup> Although mechanical telegraphs are still retained for the main signals for manœuvring the vessel, establishing com-



Electric Engine Telegraph Receiver.—One of these instruments is located in each engine room [and connected with transmitter on bridge, in conning tower, and in central station.

munication between the bridge and the engine room, yet electrical instruments parallel them and perform all other means of communication. Between important stations the electrical signal is also associated with the voice-tube. Electrical telegraphs were designed first for the use of small electric lamps illuminating orders or numbers marked upon a transparent dial. Various methods of actuating armatures by means of magnets have been experimented with, and some of these have been tried

<sup>&</sup>lt;sup>a</sup> Wireless telegraphy and telephony should be mentioned in this connection because of the general interest in this application. As such apparatus requires the use of alternating current, the suggestions in this paper are advantageous.

with uncertain success; but no instrument employing a "step-by-step" motion would seem serviceable for this duty. The accidental interruption of the supply or failure in some one indicator would affect the synchronous operation of all the indicators, thereby defeating the purpose of the signal. So development to-day is on the motor principle, with instruments designed for either direct or alternating current. Neither of these systems has been in service long enough to judge of their respective merits; but such apparatus, if of equal reliability, will succeed the lamp type by virtue of the reduced installation cost and the avoidance of "no signal" caused by defective lamps.

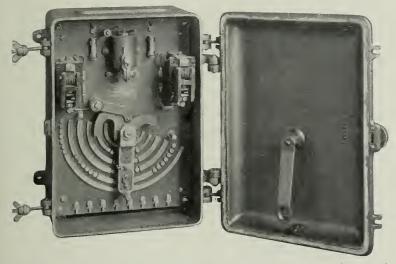
Before passing on to the subject of distribution it may be of interest to note the reduction in weight of electric auxiliaries that would come about from the suggestion made above to replace the direct-current motors by alternating-current motors. Only an approximate comparison can be given between a 125-volt direct-current equipment and a 230-volt alternating-current equipment. The former apparatus having been in service for years, and the latter not yet applied, requires that we use the weight of alternating-current land apparatus, judiciously increased to compensate for marine service. We find that the weight of direct-current apparatus amounts to 890,000 pounds, and that of the alternating-current apparatus 690,000 pounds, making a difference of 200,000 pounds, or approximately 89 tons.

## SYSTEMS OF DISTRIBUTION AND METHODS OF INSTALLATION.

For many years England held closely to the single-wire ground-return system; but to-day the ring system is in favor. This is only used for lighting and minor power circuits, and could hardly be extended to the larger power applications, because it does not admit of sufficient control to conveniently manipulate the generators. The main circuits pass from the switchboard along one side of the vessel around to the other side, returning again to the switchboard. These feeders are broken by section boxes, from which sub-circuits are led to distribution panels for the branch lighting circuits. Other nations prefer greater control for lighting purposes and hold to the 2-wire system with group feeders. These feeders are further subdivided into mains terminating at distribution panels equipped with switches and fuses, from whence are led away branches

to groups of lights. In this way separate feeders are designated for battle purposes only and others for ordinary lighting, in order that there may be no possibility of the misuse of light during a night engagement. Naturally, where two direct-current voltages are used the system would be a 3-wire one, employing the one outer and the neutral for lighting and the two outers for power.

In a proposal for 3-phase, 230-volt alternating-current distribution three wires would be used for all power circuits, and

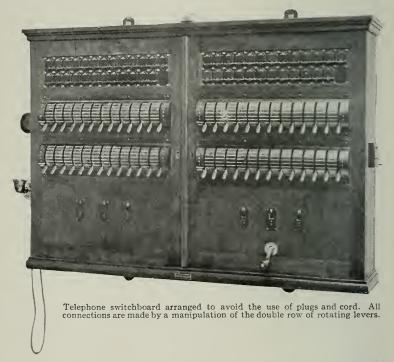


Interior view of field-control motor panel, showing again the compactness of construction, method of insulation, and the mechanical construction necessary for providing manipulation without removing cover.

the lighting could be taken from one phase so as to retain the low-potential incandescent lamp. There seems to be no reason, however, why the 230-volt tungsten lamp should not be employed with advantage. As battleships have increased in weight and dimensions they may grow to such size that requirements for higher potential will become a necessity, and then the three-phase distribution will be more economically accomplished by using four wires with resultant flexibility.

The methods of installation for marine service differ considerably when comparing the practice of the various nations. England uses lead-covered cables fastened directly to the bulk-

heads and decks by brass clips; Germany uses a lead-covered and steel-armored cable; and until recently our navy held firmly to a conduit system lightened by running well-protected leads without any covering over the rubber or braid, supported on porcelain insulators. Where any danger existed due to mechanical injury the cables were encased in steel. Foreseeing the advantages to be gained by the use of lead-covered, steel-armored cables, our navy has now adopted this construction for all future ships of the line.



For 2-wire distributions, either alternating current or direct current, this type of construction permits the use of twin conductors up to and including 60,000 C. M. Beyond this size single conductors of the same design are employed. In considering the 3-phase alternating-current system, 3-wire cables with lead and armor are prepared in order to obviate induction in interior-communication circuits and to prevent the effects of self-induction. It is not believed that, in the usual runs on ship-

board, the reactive effect of the steel braid will be harmful. If we increase the voltage from 125 to 230 volts and then compare the advantages of the alternating-current, 3-wire, 3-phase system, although we must take into consideration the power factor, we will find a large saving in weight, accompanied by a corresponding reduction in first cost of installation.

On two equal systems changing from a mixed conduit and "open-wiring" installation to that of steel-armored, lead-covered cables we find about an equal cost of installation at the present time, due to the lack of development of the art, and also to the necessity of skill in the working of this material on the vessel. A few years of practice, coupled with the design of proper tools, will reduce the cost in favor of steel-armored, leadcovered cables. Decidedly the largest gain and best reason for its adoption are the reduction in cost of maintenance and the freedom from grounds. Reports of vessels so equipped now in service for the past 17 or 18 years confirm the opinion that grounds will be found only at connection points, and can thus be eradicated altogether or at least reduced to a minimum. figures always attract attention, a comparison of the weight of several of the methods herein discussed may be interesting. These results must be approximate, because no two vessels are ever exactly alike in their equipment; but, in order that a fair comparison might be submitted, the writer has based these calculations upon a general type of equipment and computed the different proposals upon this type without considering specific changes.

Installation of cables encased throughout by conduits........461,000 pounds. Installation of mixed conduit and open wiring.................353,900 pounds. Installation of lead-covered, steel-armored cables................281,500 pounds.

This indicates a saving of 81 tons in favor of steel-armored, lead-covered cables over a full conduit installation; and a saving of 32 tons in favor of steel-armored, lead-covered cable over a mixed installation of open-wiring and conduit. This saving of weight by the use of steel-braided, lead-covered cables will be greatly increased as the manufacturers become more proficient and when deductions can be made from results gained in service.

Vol. CLXXVI, No. 1052-14

#### PROPULSION BY MEANS OF ELECTRICAL COUPLING.

A lengthy discussion of this subject is not to be undertaken in this paper. The various methods proposed to-day have been collected in one volume by Mr. H. M. Hobart, and those interested would do well to consult this little book. At the end of this volume a description of Mr. W. L. R. Emmet's system is given, with developments up to the year 1911. In a paper presented by Mr. Emmet before The Franklin Institute this year he disclosed advances that are more than ever encouraging and more than ever indicative of the future. And as it is this future which this paper is dealing with more particularly, stress should be laid upon Mr. Emmet's improvements. Briefly, he has succeeded in designing a high-speed turbine with an efficiency of 73 per cent.; he has designed a motor which may be reversed at full speed and full load without the use of external resistance; and he has brought the water rate down to a penalized guarantee of 11.5 pounds per shaft horsepower in the application to the U. S. collier Jupiter.4

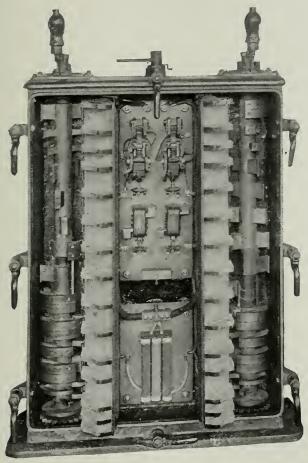
It is generally agreed to-day that for this purpose alternating current is better adapted than direct current. Therefore, the suggestion is here made that the war vessel of the future, or the real modern battleship, will be one in which the electrical equipment will assume the proportions of a good-sized central station; and many of the problems encountered in this practice on shore will have a like value on board ship. One important way that this problem will differ Mr. Emmet has pointed out, and that is, that the load will be constant, so that the power re-

<sup>\*</sup> Mr. Emmet advises that in a large battleship installation with 260 pounds steam pressure, 28 inches vacuum, and 50 degrees of superheat, the water rate per shaft horsepower would be less than 10 pounds.

It should be noted that in Mr. Emmet's proposed system of electric propulsion the main turbine speed varies with the desired speed of the ship, and could not, therefore, be used for a source of power for driving auxiliaries.

<sup>&</sup>lt;sup>5</sup> Messrs. Donnelly and Orrok, in a paper presented before the Society of Naval Architects and Marine Engineers, November, 1912, proposed a central plant for the production of electricity, and the use of this power for propelling excursion steamers. They touched briefly on the important advantage of the utilization of this power when conditions would not permit the use of the vessel. When applied to a battleship these proposals assume a greater importance.

quirements will be established and the machinery designed for a flat rating. We will then have a central station in the vessel with a capacity from 26,000 to 30,000 kilowatts. This station will be designed and equipped with apparatus so that it may



Boat handling controller with cover removed, showing double drum, one for controlling the two motions, either rotating or hoisting, or boom-lifting or hoisting, as the case may be. Note compactness of design and method of securing water-tightness.

supply both the energy necessary to propel the vessel as well as that required for auxiliaries. It is believed that the equipment will be more economically and reliably handled by an alternating-current system, and the efficiency of the engineering greatly improved.

#### CONCLUSIONS.

The proposed use of alternating current on shipboard is not new. Mr. F. O. Blackwell read a paper before the Society of Naval Architects and Marine Engineers at a meeting held in New York City, November, 1902, in which he proposed the use of a 3-phase, 3-wire, 220-volt system and outlined its advantages over the 2-wire, 125-volt direct-current system. It is interesting now to note that he advised the use of turbo-generators instead of the then customary reciprocating engine for driving dynamos. For the last eight or nine years we have employed the turbine for this purpose.

In The Journal of the Naval Institute, No. 138, will be found an article by Lieut. S. N. Robinson, U. S. A., giving ample reasons for the employment of such a system on our modern war vessels; and in the February number of The Journal of the American Society of Naval Engineers appeared a detailed paper by Lieut. A. Norris comparing the advantages of a 230-volt alternating-current system with the present standard 125-volt

direct-current system.

The possibility of electric propulsion and the increase in motor applications take us beyond these low potentials and away from the advantages of direct current. If satisfactory service is given by the use of 2200 volts alternating current for the propulsion of the vessel, there could be no reason forbidding its use elsewhere in the ship. At this potential direct current would react detrimentally on the hull structure and would not provide the flexibility inherent to alternating current. The ease with which alternating-current voltage may be reduced will restrict the distribution of high potential to those portions of the vessel where it may be cared for with safety. Concisely stated, alternating current affords the economical production of power in large quantities at high pressure, accompanied by a flexible system of distribution.

Peanut Butter. W. R. BEATTIE. (Bureau of Plant Ind. Circular 98.)—This is a brief account of the manufacture of peanut (earthnut) butter, a food product consisting of fresh roasted peanuts ground finely and flavored by adding salt. It is estimated that in 1911 approximately 1,000,000 bushels of the shelled nuts were used for the manufacture of peanut butter in the United States.

## THE DEVELOPMENT OF THE TALKING MACHINE.\*

BY

### EMILE BERLINER,

Member of the Institute.

To receive the commendation of The Franklin Institute in recognition of endeavors relating to technical or scientific developments should in itself be ample reward for satisfying the higher aspirations of the engineer. Those in particular who appreciate the high standing of the Institute before the world and the eminence of the men that are its leaders and compose its committees will always be profoundly gratified when they are favored by the awards with which the Institute vouchsafes its good opinion. Needless, therefore, for me to assure you how grateful I am because it has been my good fortune to labor in promising fields and because I was able to win your expressions of approval.

Nor is it the first time that the Institute has invited me here to speak in this hall. It was twenty-five years last week that I gave here the first public exhibition of the gramophone and read a paper describing its then short history and its processes.

On that evening of May 16, 1888, I showed in this auditorium how a voice could be etched into metal, and, while the etching was being done, I rendered a programme of songs, recitations, and instrumental solos previously prepared which, crude as they were, presaged the possibilities of more perfect results for the future. These disk records, the first of their kind, were reproduced on a machine turned by hand, and all of them were originals. One duplicate was shown and reproduced, and this had been made by electrotyping an original sound etching in the same manner as an etched halftone is electrotyped. It was, however, easy to foresee the vast possibilities of the invention, and under the paragraph "Practical Applications" I ventured the following predictions:

<sup>\*</sup> Presented at the stated meeting of the Institute, held Wednesday, May 21, 1913, when Mr. Berliner received the Institute's Elliott Cresson Medal, in recognition of his contributions to telephony and to the art of sound-reproduction.

A standard reproducing apparatus, simple in construction and easily manipulated, will, at a moderate selling price, be placed on the market.

Those having one may then buy an assortment of phonautograms, to be increased occasionally, comprising recitations, songs, chorus, and instrumental solos or orchestral pieces of every variety.

Prominent singers, speakers, or performers may derive an income from royalties on the sale of their phonautograms, and valuable plates may be printed and registered to protect against unauthorized publication.

Collections of phonautograms may become very valuable, and whole evenings will be spent at home going through a long list of interesting performances.

Languages can be taught by having a good elocutionist speak classical recitations and sell copies of his voice to students. In this department alone, and that of teaching elocution generally, an immense field is to be filled by the gramophone.

Addresses—congratulatory, political or otherwise—can be delivered by proxy so loudly that the audience will be almost as if conscious of the speaker's presence.

A singer unable to appear at a concert may send her voice and be represented as per programme, and conventions will listen to distant sympathizers, be they thousands of miles away.

On that evening the status of talking machines was as follows: The tinfoil phonograph of Edison had been known for ten years and was a scientific curiosity only, though of historic value. The wax cylinder phonograph or graphophone of Chichester Bell and Sumner Tainter had been invented, and its aim, as pronounced by its promoters, was to become a dictograph for private and business correspondence. Both machines represented a system of sound recording in which sound waves were either vertically indented, as in the Edison phonograph, or vertically engraved into a wax cylinder, as in the Bell-Tainter graphophone. In reproducing these records a feed screw was provided which turned either the cylinder past the needle or the reproducing sound-box past the cylinder.

The gramophone changed all this. Its record was made horizontally and parallel with the record surface, and by itself it formed the screw or spiral which propelled the reproducing sound-box, so that while the needle was vibrated it was at the same time pushed forward by the record groove, and, as the sound-box was mounted in such a manner that it was free to

follow this propelling movement, it made the reproducer adjust itself automatically to the record.

I pointed out at the time that the horizontal record of the gramophone was better capable of recording sound in its entirety, while in the vertical record of the phonograph-graphophone a certain distortion took place which became more pronounced the deeper the sound waves indented or engraved the record substance.

When I returned from this exhibition to Washington I set to work trying to develop a duplicating process which should enable me to make any number of records of the same selection in hard, wear-resisting material, like celluloid or hard rubber. The first successful duplicate so produced was made for me in the same year in celluloid by Mr. J. W. Hyatt, well known to you as one of the inventors of celluloid, and this duplicate is still in existence (now in the National Museum in Washington), being the first sound-record duplicate in hard material which was made by pressing a reverse of the original record into hard material while the latter was softened by heat, and then chilling it while still under pressure. This process is at the bottom of the present industry of making many millions of sound-record copies annually.

The trouble I found with celluloid was that it was not quite hard enough for the gramophone system, and I therefore turned my attention to hard rubber. After several years of experimenting, trying to make accurate electrotyped reverses or matrices from original zinc records, so that the very surface, even to its microscopic details, should be copied, I finally succeeded and, with the help of a rubber company in the Middle West, to make large numbers of accurate copies from a matrix, and soon afterward I launched the disk talking machine on the market.

By 1895 the invention was so far perfected that it began to gain many admirers by its simplicity and ease of manipulation. But it soon developed that many rubber records were imperfectly pressed and showed flat places, and the rubber company was unable to correct this part of its work and furnish a reliable output.

In this emergency I remembered an attempt made by the Bell Telephone Company in 1879, while I had charge of its laboratory, to substitute a shellac composition for the hard

rubber of which its hand telephones were made, and I got in touch with a factory that made electrical fixtures of such composition. I gave them a nickel-plated copper matrix of a record, and the first copies they pressed from this matrix in shellac composition showed remarkable uniformity, and, moreover, because the material was harder than hard rubber, the reproduced sound was louder and more crisp. These composition duplicates proved at once a great success, and ever since shellac composition has been used for making disk records, although recently attempts have been made to employ for them a substance like bakelite.

As early as 1887 I had tried to make records by pressing a matrix into sealing wax, and it is interesting to realize that these modern composition disk records are in reality seals of the human voice, because the substance they are made of is a modified sealing wax, both containing shellac as a basic substance. Few people have a conception of the untiring efforts which have been made year after year, and still continue, in order to obtain a composition which will answer all the requirements necessary for resisting the wear of the needle or prevent the latter from being ground blunt too fast. If the material is too hard and gritty it will wear the point of the needle, so that before the end of the record is reached the reproduction becomes weak and blurred. If the material is too soft the record groove will quickly wear rough and the record reproduction become scratchy. Shellac is much adulterated, and the mineral and fibrous substances which are added require careful selection, and this whole department is in the hands of experts who do nothing else all the year around but test the substances and the mixing processes which are employed for producing record material.

Of recent years Mr. Joseph Sanders, of Washington, D. C., has perfected a record disk having a solid fibrous core which is faced on both sides with a very thin layer of shellac composition of a superior quality. Records pressed in such disks are remarkably smooth, and withstand climatic changes better than the others, so that they may be sent to the tropics without danger of being affected by the combined heat and moisture which abounds in those parts of the world. Moreover, these disks are light in weight and have sufficient flexibility to successfully withstand careless handling and breakage resulting therefrom.

After the hand-driven gramophone had been on the market for a few years the company which had been organized for exploiting the invention secured the co-operation of Mr. Eldridge R. Johnson, now the president of the Victor Talking Machine Company. An able mechanician and of shrewd technical perception, Mr. Johnson succeeded in developing a motor-driven reproducing machine which ran with great regularity of speed, was readily adjustable, and, last but not least, ran silently so as not to disturb the sounds of the record by its own noise. Such a motor machine had been made by a New York clockmaker as far back as 1801, but had not been quite noiseless at that time. Mr. Johnson also took note of the fact that the patents of Bell and Tainter covering the method of cutting a sound record in wax were approaching their final term of legal existence. He decided to take advantage of this circumstance and applied himself to the abandoning of the difficult etching process and of combining the much easier wax-cutting technique of the graphophone with the gramophone method of horizontal recording. He, of course, adhered to the automatic reproducing, to the disk form of record, and to the method of duplicating disks by impressing an electrotype reverse or matrix into shellac composition under heat and pressure.

We strike here an experience parallel to that which occurred in the early development of the telephone when two independent systems—the magneto transmitter and reproducer and the loose-contact transmitter and reproducer—were combined to form a system superior to either alone, when the loose contact was finally used as a transmitter and the magneto telephone as the receiver for telephonic intercommunication, the system which has been in use ever since.

In a similar manner Mr. Johnson took from the graphophone the recording in wax and added it to what the gramophone already had, and thereby produced the modern gramophone, also known as the Victor talking machine, Disk Graphophone, Columbia Phonograph, and other trade names.

And the machine which hitherto had confined itself to popular musical talents, to low comedy, simple songs, cornet and clarinet solos, and to military music, rapidly improved to such a degree that it began to appeal to grand opera stars, to the great masters of the piano, to the wizards of the violin, to

symphony orchestras, to virtuosos on every kind of musical instrument, and to celebrated actors and elocutionists. The gramophone repertoire expanded to comprise the whole gamut of audible phenomena, and musical reproductions in particular became so startlingly perfect that big hotels and restaurants were able to have their orchestras accompany the great singers of the day as they appeared by proxy out of the horn of the talking machine.

The predictions made before this Institute in 1888 were being fulfilled even to the application of the gramophone to national politics. Last year the speeches of the three presidential candidates were heard and reheard all over this country, and the recognition of the individual voices—something I had noticed in the very first gramophone records—was one of the notable characteristics of these speeches. The speakers were present in all but their bodies: the proxies were complete.

And down in extensive fire-proof vaults, built by the big companies here and in Europe and securely closed to all but a few trusted employees, are stored away the copper or steel matrices, the indestructible and precious legacies which the masters of song and performance are leaving to future generations. Their immortality is secure because the very air pulses which smote the ears and brains of their own generation are already being resurrected above the graves of those who have died.

What had in the meantime become of the cylinder machines? The graphophone or wax cylinder phonograph, true to its original programme, had developed into a most serviceable dictograph, and it is astonishing how much time and trouble is saved by such a machine to the business manager, to the press reporter and to the chief of office. Instead of calling for the stenographer just when the latter is perhaps busy transcribing from her notes on the typewriter, the manager takes one wax cylinder after another and dictates his letters or orders to the lifeless machine. He may do so in his leisure moments, immediately as a thought strikes him, and when the rack of wax cylinders has been loaded with his dictation or orders, he rings for a boy, who distributes the cylinders among the typewriters. These in turn place the cylinders on reproducing machines and with ear tubes over their heads and with nimble fingers on the

keys they transcribe from the talking record, now stopping to repeat a sentence, now taking notes of special orders with which the manager has interrupted his letter dictations. No time is lost in waiting; the strenuous life has permeated from the corporation manager to the most distant workers of his will, and the high speed of modern machinery has a counterpart in those wonderful combinations of money and brains which grind out twentieth century enterprise in the steady flow of a rushing stream and as a continuous performance.

Thus does modern technical science in all its branches fill the pressing demands of an eager humanity even to overflowing. But a hand is raised in protest, and out from a misty past there looms up an ancient landmark of human history, an achievement of an earlier civilization. It is the Day of Rest, when tired brains turn to the woodland and the mountain stream, to green fields and meadows, and to the low song of birds, the chirping of crickets, and to the call of the whip-poor-wills, who decline to perform for talking machines and who, like some other ideals that appeal to the romantic within us, must be pursued before they will yield to us the rewards of their charms. Machines may give us talk and melody, light and comfort, speed, and even flight, but they will never give us life's poetry. And it is well that it be so.

The companies making cylinder machines soon began to observe that wax cylinders also contained possibilities as means of amusements, and they set to work invading this apparently profitable field of application.

Their principal problem consisted in finding a proper process for duplicating from the original cylinder record. The best method appeared to be that of the gramophone, namely, make an electrolytic negative or cylinder matrix from the original record and use this as a mould for casting duplicate cylinders. Unfortunately, however, cylinder records do not lend themselves readily to such a process. To deposit metal on the wax cylinder was easy, and the producing of a good negative or mould appeared to be a very simple matter, because the wax record was simply melted out of the copper shell, leaving on the inside a reverse of the sound waves. But, having produced this mould and pouring into it a cylinder of copy wax, it was difficult, and at first impossible, to separate the copy and get it out of the mould.

So for a time they abandoned this method and developed a mechanical duplicating machine in which, by means of a carefully-mounted lever, having a tracing point on one end and a cutting point on the other, the record was transcribed from the original cylinder upon duplicate blank cylinders, and this system was used commercially for a number of years with a certain degree of success.

However, the laboratories of the several cylinder factories continued experimenting with the electrolytic method, and finally they produced a wax for casting the duplicate cylinders, which on the application of cold would sufficiently contract inside the copper cylinder as to permit the duplicate to be slipped out. This obstacle having been overcome, it was then found, however, that the matrix or mould did not represent the original record in all its perfection, but had lost in quality and surface because of the brushing with graphite necessary for making the original wax surface electrically conductive.

This difficulty was finally overcome by Mr. Edison through the development of a so-called process of gold moulding. This consisted in passing a high-tension current through a vacuum in which the wax cylinder record formed one terminal and a gold anode the other. Infinitesimal particles of gold are thereby transferred upon the surface of the wax record until it is entirely covered, and it is then placed in an ordinary copper bath and a good thickness of copper deposited over the gold, after which the wax is melted out.

Such a mould is a perfect reverse of the original record, and it enabled the Edison Company to place upon the market complete assortments of cylinder records in competition with the gramophone or Victor disk records.

While I cannot admit that such phonograph-graphophone records ever came up to the expectations of the most critical, they satisfied thousands of people who appreciated the fact that, in reproducing these records of a softer material, they were not obliged, as in the gramophone, to change the needle with every record, since wax or even celluloid does not wear a needle as rubber or shellac composition does.

Of the many minds working on talking machines, some presently turned to the very natural idea of producing records of the phonograph up-and-down system in disk form. This was

not new, but had never been developed. The advantages were obvious, because disks can be duplicated easier than cylinders and can be made in hard materials which could be more easily handled and occupied less space.

The first commercial disks with phonograph up-and-down recording were placed on the market by the firm of Pathé Frères, the well-known cinematograph and film manufacturers in France. The method employed by this firm, however, was not the simple one of recording sound into wax disks and then duplicate by the same method as employed in the gramophone. Pathé, owing to some technical difficulties in direct recording, first recorded on a very large cylinder of about 12 inches diameter, after which they mechanically transferred this record to a wax disk by means of a system of levers, and from this disk they developed a matrix in the usual manner.

Recently, however, the Edison Company has been recording phono-vertical records directly into wax disks and then following the gramophone method of duplication. We have, therefore, on the market to-day disk records not only of the gramophone type where the sound waves are of even depth and vary horizontally, but also those of the phonograph-graphophone system in which the sound waves are represented by corresponding variations only in the depth of the record groove.

On the theory developed by me twenty-five years ago, that a vertical record must distort the original sound in proportion to the depth of indentation or cutting, we have then arrived at a point where a phonograph-graphophone or vertical record in disk form may closely approach the perfection of a horizontal or gramophone record, provided the phonograph record is cut extremely shallow. In this condition, however, the record groove cannot readily guide or propel the stylus, and it requires a feed screw for propelling either the disk or the sound-box. It has been tried to first cut a plain spiral groove, deep enough for propelling the stylus, and then superimpose at the bottom of this groove a phonograph-graphophone record, but this method has shown sufficient difficulties for preventing its introduction up to the present time. The gramophone type of talking machines still prevails, and every year brings it closer to a fidelity in recording and duplicating which should satisfy the most exacting critics. The celebrated stars of grand opera would hardly

entrust the keeping of their voices to any talking machine except they felt that the records represented their art in a satisfactory manner.

And such is the status of the talking machine at the present time. Considered critically, the principal further advances should be the making of disk records in a material of the character of glass or hardened steel in which they would retain a polished surface indefinitely and which, on account of great hardness, would prevent the slightest loss in the most delicate vibrations recorded on the original disk. Bakelite would appear to be a promising substance, but it needs adaptation to requirements which escape the chance observer.

In the mere mechanical part of talking machines an electrically-driven reproducing disk machine generally introduced would undoubtedly commend itself to a discerning public. Such an electrification of disk talking machines, by relieving the present hand-organ energy, would make for an increase in æsthetic enjoyment such as the promoters of talking machines are ever anxious to secure for their products.

Before closing this paper mention should be made of that very ingenious device, the telegraphone, developed by Mr. Poulson, of Denmark. In this instrument telephone sound waves are made to record themselves as localized magnetic fields of different lengths and intensities in a steel wire, on a steel tape, or as a spiral record on a steel disk. In the reproduction these magnetic fields, by passing in touch with a small electromagnet, cause electric undulation corresponding to the original sound waves in the helix of this magnet. The circuit of the helix includes a telephone receiver, which then emits the sounds originally spoken into the telephone transmitter.

Beautiful as this system appears to be, it suffers from the inherent fault that you cannot confine a localized magnetic field representing a sound wave as you can define a mechanical record of the same. As a consequence articulation is impaired because the magnetic halo of one wave superposes the halo of the next, and this is fatal to those delicate overtones which form the essential characteristics of most consonants. To remedy this the linear speed of the record was increased, but it then became cumbersome on account of too great length, and it still showed

losses in articulation because of the several electromagnetic transformations which are embodied in this system.

Magnetic fields were long ago localized in the well-known experiment of writing with a magnet on a piece of steel and then strewing iron filings over it, when the writing appeared as lines of iron filings which stuck to the magnetic tracings. The first who proposed to apply this principle to the recording of sound by fixing telephone undulations on a steel ribbon or wire and cause such a magnetic record to induce telephonic undulations by magneto-electric impulses and reproduce the original sound was Mr. Oberlin Smith, now of Bridgeton, N. J., who published this idea in a prominent electrical journal some years before the advent of the telegraphone. Mr. Smith himself, however, did not carry the plan into successful execution, and I do not know whether Mr. Poulson knew of the Smith publication when he took up and successfully completed the telegraphone.

The instrument remains to-day a beautiful demonstration of electrical and magnetic phenomena as applied to the transmission, recording, and reproduction of speech, but its ultimate development into as perfect and practical an apparatus as the mechanical talking machine appears to be is precluded by the existing conditions.

We have in one of our offices a photograph which one of our travelling salesmen brought back from a business trip to the trade centres in the wilds of Canada. It shows a giant lumberman reposing placidly on a rough bench in front of his crude log cabin. Nothing but forest and mountains surround him. His axe and his shotgun lean against the cabin within easy reach, he is smoking his pipe, and his faithful dog crouches at his feet. His nearest neighbors are miles away, and in days gone by the solitude of his existence would have been but rarely relieved by diversions or pleasures, and then only by occasional visits to the centres of supplies, where barrooms, gambling dens, and low dance halls satisfied his yearning for a change from his laborious daily life.

But now there stands in front of him a rough dry-goods box, and on it he has placed an old-time horn gramophone and a stack of disk records. The concert halls, the vaudeville and opera houses of the world are represented in that pile; English statesmen and American Presidents may talk to him as if face to face, and he can entertain his occasional visitors with the same choice selections that are heard in the drawing-rooms of mansions occupied by the favored few, be they of the capitals and metropoles in the far away.

We framed that picture and wrote under it the words "In

Touch With Civilization."

Close-plated Platinum Utensils. Anon. (Brass World, ix, 3, 84.)—The high cost of platinum has led to many experiments to produce cheaper platinum vessels. Byron E. Eldred, of Bronx-ville, N. Y., has taken out various patents for close-plated platinum dishes, crucibles, and other apparatus used in the chemical laboratory. The platinum is welded to a base of steel or nickel and then rolled into a sheet, which is then spun into the desired shape. The surface is thus coated with platinum, but the edges are exposed base metal. To cover these up, platinum is fused on the edges, and thus an article is obtained completely coated with platinum but at a much less cost than a solid platinum vessel. The interior of steel or nickel can be made of sufficient thickness to make the articles quite stiff and rigid if desired.

Prevention of Leakage in Steam Metal Valve Castings. Anon. (Brass World, ix, 3, 79.)—Valves are tested after finishing at various pressures, according to the work for which they are intended, by hydraulic pressure, air, or steam, to ascertain if there is any leakage. Brasses and bronzes are equally liable to leak. Leakage is not caused by any lack of tensile strength, but by the presence of dross, by blow-holes or other imperfections in the metal, that is to say, it is a matter of foundry practice. The causes of leakage are: (1) pouring the metal too cold; (2) too short gate; (3) oxidation of the metal in melting; (4) walls of valve too thin; (5) aluminum in the metal; (6) sulphurizing of the metal during melting; (7) core-box or pattern badly made, so that the casting is thick on one side and thin on the other; (8) wrong metal mixture; (9) gated in wrong place; (10) use of large quantity of phosphorus as a deoxidizer; (11) too little tin in the mixture; and (12) sharp corners on the pattern. The presence of dross (oxide) in the metal is the cause of nearly all leakages.

## THE IMAGINATIVE FACULTY IN ENGINEERING.\*

BY

## ISHAM RANDOLPH, D.Eng.,

Member of the Institute.

"We had visions, oh! they were as grand As ever floated out of fancy land,"

are words sung by a poet of our own land to the ears of a few who knew, honored, and loved the singer. He sang of "The Lost Cause" with a beauty and a pathos that touched the hearts of all who mourned for the men who followed that "conquered banner" along the path that led "to glory and the grave."

The sculptor beholds in blocks of marble forms that are hid from his fellow-men, who see only a mass of stubborn stone. The explorers of Olympia have resurrected from the detritus which buried them treasures of Grecian art wrought from the marbles by Phidias, Praxiteles, and others whose chisels made Greece beautiful and themselves famous. Within our own time one of our own race and nation saw in a marble block an imprisoned form and day by day, with mallet and chisel, he toiled to liberate the loveliness of face, torso, and limb that duller eves could not see, but which the opaque covering could not hide from him. The encasing stone must be removed carefully, skilfully, gently, that the fair brow might not be scarred nor the delicate outlines of the face, form, or limb be marred. Little by little the revelation which, from the first, was so clear to the sculptor came to his dull-eyed fellows, and at last the Greek Slave came forth in all of her womanly beauty to delight the human vision until she, too, shall some day be buried, like the wonderful creations of Praxiteles, in some overwhelming convulsion of Nature.

It is not, however, of the poet's inspired imaginings nor of the revelations of the sculptor's art that I am to speak, but of

<sup>\*</sup> Presented at the stated meeting of the Institute held Wednesday, May 21, 1913, when Dr. Randolph received the Institute's Elliott Cresson Medal, in recognition of his achievements in civil engineering.

the "Imaginative Faculty in Engineering," for the engineer, no less than the sculptor, sees things that are hid from other eyes than his.

What has not God revealed to the sons of men when He has drawn aside the veil and let the thing that is to be cast its reflection upon the mirror of imagination? Away back in the ages when the children of Israel were wandering in the Wilderness it was disclosed to their Moses that a tabernacle must be created as the centre to which the worshippers of the Most High God must gravitate, and to him was revealed the form, the fashion, and the adormment of this "temple made with hands," and the final command, after all had been shown to his mental vision, was: "And look that thou make them after the pattern that was shown thee in the mount" (Exodus xxx: 40).

A man's first conception of anything which ought to be created is his vision, the revelation which impresses itself upon his imagination with a reality that enables him to reveal it to others, either by word-painting or by graphic delineation which, after taking form, must be given substance. Giving the substance to the form involves knowledge, knowledge of materials, knowledge of the strength of materials, the ability to determine dimensions which must be used to give sustaining power to the substance which has taken the form revealed to the imagination.

The vision does not always come complete in its revelation. First it may be dim, "seen through a glass darkly"; partiallyobscuring mists hide all but a suggestive glimpse of the thing that is to be, but that suggestion is grasped by the imaginative faculty, and the eye of the mind gazes earnestly, waiting for the passing of the mist and the perfect unveiling of the vision. How many of earth's monuments which now stand to the honor of the engineer and render useful service to mankind had their genesis in imagination! Take some mighty suspension bridge whose graceful catenary is not distorted by loads which would bend a Titan's back, and, as you gaze upon it, think how it came to pass. It supplies a need, a great need; multitudes felt the need, but the way to supply it was not given to the multitude. One among them all saw the vision. He saw the great river flowing by; he felt that the bank on which he stood should be joined to the farther shore; but how? His imaginative faculty began to work. Here and over vonder he would dig down into

the soil until he reached a stable base; in the pits so sunk he would lay firm foundations upon which he would rear towers, high and strong. Inland from these towers he would plant massive anchors of masonry; from the anchor on the hither shore to the anchor on the nether shore he would pass cables over his high towers, cables that sagged between the towers, and from these, by rods, graduated in length, he would suspend beams, and on these beams he would lay his flooring; all of this was pictured by his imagination. From that picture, as he saw it, he made a material transference which could be seen by his fellow-man. He called his fellow-man, skilled in the knowledge of engineering science, to his aid, and form and proportion were developed and the necessary strength for every part was computed. The cost was figured out, and all that could be known in advance about the bridge that was to be was laid before the rulers of the people. The plan was adopted; deep down to an enduring base the foundations were carried by men whose strength and toil rear all of earth's structures, be they perishable or enduring. Those skilled among them in the arts of stereotomy builded the masonry strong and high. In the works where ore, dug from the mines, is melted and fused by coal dug from other mines, the members, of mighty section and prodigious strength, are forged and fabricated. In other works, the wires that in union will make the strength of the great cables that shall stretch across the stream are being drawn. Trees of centuries' growth, felled in far-off forests, are being sawn and fashioned for their place in the work, and when all is ready the multitudinous parts are assembled, the cables are made fast to their anchorages and lifted to their saddles on the tops of the towers by machines which—like the work which they are set to aid in creating—had their beginning in the imagination of man. By and by, all is accomplished, and two tides of humanity ebb and flow across the mighty bridge which had its genesis in the imagination of a man.

No river sways such power for good to the whole land if made amenable to human control, and no river in the land is so terribly devasting in its unbridled power, as is the Mississippi. Against its encroachments men have raised barriers, broad and strong, only to have them undermined and engulfed by the onsweeping waters.

204

This river, for scores of mile's before it pours its sweet waters into the brine of the Gulf, is wide and many fathoms deep; but for uncounted centuries it has been transporting soils, filched from its banks, and depositing them at its mouth; building land out into the Gulf, and finally crossing barriers of its own construction, not by one channel, but by many. No one of these channels was deep enough to permit ocean-going vessels of the larger class to enter the deep, wide water that came down from the north and then flowed by shallower ways over the barrier and out to sea, and so commerce upon the river was only for river craft, and cities which were waiting for their upbuilding for the coming of the world's commerce had to sit beside their incipient docks and wait. Governmental forces had worked and were working ineffectually upon the problem of opening up "the passes." About the year 1875 a man with a vision came to the Government with a plan to secure deep navigation across the bars that closed the mouth of the river. The engineers of the Government were told of the vision, but the dreamer could not impress them with his faith. They perhaps had not seen, as he had, what had been done with a river in the old land. The Government would not take any risk to open the Mississippi. but Eads—the man with engineering imagination—so impressed his vision upon men of means that they guaranteed his proposal to the Government, agreeing to put up all the money and take all the risk, provided the Government would reimburse them when success was demonstrated and deep-draught vessels could enter and leave the Mississippi without hindrance. This man saw in his vision two lines of jetties constructed of willow mattresses weighted with stone, laid parallel to each other and a thousand feet apart. These, in his mind's eye, grew in height and length until they stretched from deep water up stream to deep water in the Gulf. He saw the waters as they flowed down to this contracted channel pile up until they attained a head sufficient to give them the necessary velocity to carry through the reduced cross section the volume which had flowed sluggishly through the wider way. He saw the velocity impart erosive energy to the waters which impinged upon the sand of the bottom of this new channel; each eroding drop of water picking up its grain of sand and carrying it along until, emerging into the unlimited area of the Gulf, it lost its energy and dropped its load. Thus myriad

drops of water carried myriad grains of sand, and every grain removed tended to deepen the channel between the jetties. This he saw, and thus did the waters labor until they had dug for themselves a way out to the Gulf, through which they might flow unvexed, and when that work was accomplished the way was open for the "toilers of the sea" in their deep-laden craft to pass to and fro between the "Crescent City" and the sea ports of the world. The imagination wrought first and the physical results confirmed its visions.

Yonder where the waters of Niagara make their fearful leap over the edge of the escarpment and then rush madly down the gorge to the whirlpool and beyond the "imaginative faculty in engineering" has left its impress, and great works bear witness to the fact that there it has wrought mightily. Back of that awful sheet of falling water there is a pathway, forever wet with the off-flung spray; on one side is the hard wall of the escarpment, on the other the wall of green, translucent waters, the dim twilight effect made awesome by the roar of the torrent wall as it drops into the abyss—a wall forever falling but never broken. A man trod this dangerous path and he heeded not the roar, nor the mist, nor the death that might claim him should he make a false step on that slippery footing. No! he saw a vision; the imaginative faculty in engineering was aroused. His eye pierced the face of the escarpment, and he saw a tunnel open up through the rock beneath the river. His tunnel went straight to a spot in the roaring, seething waters some thousands of feet from where he stood, and there he saw a deep, long slit in the rock, rising from the up-stream end of his tunnel to a stately building. In the building there were generators carried on top of vertical shafts which were caused to rotate by turbines at their lower ends down in the bottom of that long, deep slit in the rock. All this and more the "imaginative faculty in engineering" revealed to that engineer, and the engineer made it plain to the men with money that the sublimation of his vision would make their money earn more of its kind, and to-day you may look upon the completed work of the Electrical Development Company and know that it is there because of the imaginative faculty in engineering.

Another engineer explores the canyon of a river; here it flows between granite walls that tower on either side above its rushing

waters. The walls here are not far apart, and an idea, a vision, comes to the engineer. That river at times is a torrent; the rains have descended and the floods have come and the river rushes on, a destructive agency, leaving a land behind perishing of thirst. The engineer asks himself, "To what purpose is this waste?" And again, "Why should not this waste be prevented?" And the answer comes, "It can be, and you can do it." Then he sees the way. There is the pass. He will hold the pass against the oncoming waters. The imaginative faculty is at work and shows him that deep down beneath the stream there are footings "sure and steadfast" on which he can found a dam; this dam he can anchor into the granite banks of the stream. That was a revelation; to-day there is a reality. The Arrow Rock Dam rises 351 feet above its base and the waters rush against it; they stop and swell and press, but the dam is stronger than the pressure. The floods have lost their freedom, the waste of waters has been stopped after untold ages, and to-day they are garnered and sent to make gardens in the desert; and, like Samson of old, they must grind in their prison-house and give off power which will do man's work and light man's dwellings. The voice that spake to Moses speaks to the engineer to-day: "And look that thou make them after the pattern that was shown thee in the mount."

Separation of Radio-active Substances from Thorium. F. GLASER. (Chem. Zcit., xxxvii, 477.)—Monazite sand is mixed with twice its weight of concentrated sulphuric acid and heated to 25° C. for five hours with constant stirring. When cold the mass is poured into 20 volumes of water and filtered after 24 hours. By diluting this mixture, or by adding magnesia to it, a precipitate of thorium phosphate is obtained. A better method is to dilute till the free sulphuric acid is reduced to 2 to 3 per cent. and then boil the solution, which produces a voluminous gelatinous precipitate of thorium phosphate and its radio-active derivatives. This precipitate contains thorium Y, which may possibly be identical with thorium X. To separate the thorium Y, the moist precipitate is treated with dilute sulphuric acid, or else dried, heated with concentrated acid, and poured into water. The thorium is dissolved as sulphate, leaving somewhat impure thorium Y undissolved. The half period is about four days. Thorium preparations which yielded thorium X on treatment with animonia did not yield thorium Y when treated by this method.

# A MAINTENANCE-OF-WAY DEPARTMENT RAILROAD TESTING PLANT.\*

BY

#### B. B. MILNER,

Member of the Institute.

Some time ago the writer, whose experience has been chiefly with railway motive power, was asked to assist a maintenance-of-way engineer in the investigation of a problem which involved a study of track design and the stresses imposed upon its various members.

Consultation with several men of recognized experience and authority, as well as an investigation of all experimental work performed in this connection, and a search through the literature of the subject, revealed the fact that dependable data upon which to base definite conclusions upon various points raised were lacking.

This same revelation was made by Mr. O. E. Selby, Bridge Engineer of the Cleveland, Cincinnati, Chicago & St. Louis Railway, in writing an admirable paper, entitled "A Study of the Stresses Existing in Track Superstructure and Rational Design Based Thereon," which was published in Bulletin No. 80, American Railway Engineering and Maintenance-of-Way Association, October, 1906. This paper contained several paragraphs elaborating upon the statement that "railroad track has grown in strength as heavier loads have made increased strength necessary, but such growth has been entirely along empirical lines, and not one single detail of track superstructure bears marks of engineering design."

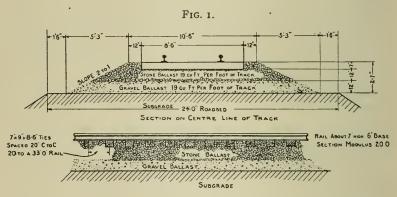
Mr. Selby, after careful consideration of such factors as rail loading and stress therein, tie bending, bearing of tie upon the ballast, depth of ballast and its bearing upon the subgrade, developed the track design shown in Fig. 1. The sizes on the drawing are for 60,000-pound axle loads. The principal sizes for 50,000-pound loads, using various weights of rail, are given in Table I.

<sup>\*</sup> Communicated by the author.

#### TABLE I.

Rail	80 pounds	90 pounds	100 pounds	Rail with Sec- Mod. 20
Axle load	, -	50,000 ' 7'' x 8'' x 8½' ' 18''	50,000 '7'' x 8'' x 8½' 20''	60,000 7" x 9" x 8½' 20"
rail Depth of ballast	24 14" stone	22 16" stone	20 I8" stone	20 { 12" stone { 12" gravel 24'
Width of roadbed	21'	21'	22'	24' gravel

From this table it is at once seen that the number of ties per 33-foot rail, as well as the depth of ballast, is much greater than that found in standard track to-day, and, since the figures



Track superstructure for 60,000 lb. axle loads.

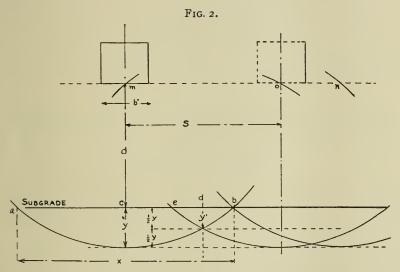
in the table are the result of a careful consideration of the strength of the materials involved, it is not surprising that the question of strengthening our present standard tracks is becoming such a live one, especially with our heavier trunk lines.

The depth of ballast, computed by Mr. Selby, was obtained from formulæ for the thickness of ballast necessary to produce equal distribution of axle loads on the surface of subgrade beneath the ballast, for which Mr. Thomas H. Johnson, Consulting Engineer of the Pennsylvania Lines West of Pittsburgh, was responsible. Mr. Johnson deduced these formulæ after studying a report, made by Railroad Director Schubert, of Berlin, in 1899, of observations extending over a period of over three years, on the action of ties actually in track. This report was translated and published by Mr. W. C. Cushing, Chief

Engineer, Maintenance-of-Way, Pennsylvania Lines, and appeared in Bulletin No. 76 of the American Engineering and Maintenance-of-Way Association, June, 1906.

In Mr. Johnson's formulæ the two following premises are made:

I. "That the width of distribution of the load is equal, for stone ballast, to the width of the tie plus the depth of the ballast, and, for gravel ballast, to the width of the tie plus half the depth of the ballast."



From Fig. 2 this premise may algebraically be expressed thus:

For gravel, 
$$x = b' + \frac{1}{2} d'$$
.....(1)  
For stone,  $x = b' + d'$ .....(2)

where x is the width of ballast pyramid carrying the load.

2. "That the intensities of pressure within that width are proportional to ordinates to an arc of a circle whose radius and chord are each equal to the width of distribution of the load."

The deduction of the formulæ is as follows:

If the circular arcs be considered as approximate parabolas, the intensities of pressure may be assumed to be proportional to the ordinates of the curves. The area of the parabolic segment  $= \frac{2}{3}xy$ , hence the mean ordinate  $= \frac{2}{3}y$ , or the mean pressure  $= \frac{2}{3}$  the maximum.

The pressure at b is o, hence, to obtain an approximately uniform distribution of pressure over the surface of the subgrade, the tie-spacing S must be such that the curves overlap and have a common ordinate y' equal to  $\frac{1}{2}y$ . This will obtain when  $db = \frac{1}{4} cb$ ;  $cb = \frac{1}{4} ab$  or  $mo = \frac{3}{4} mn$ .

Hence, the tie-spacing  $S = \frac{3}{4}x$ . Therefore, from (1), for gravel,

$$S = \frac{3}{4} (b' + \frac{1}{2} d')$$

and from (2), for stone,

$$S = \frac{3}{4}(b' + d')$$

from which the required ballast depths d' are obtained by transposition:

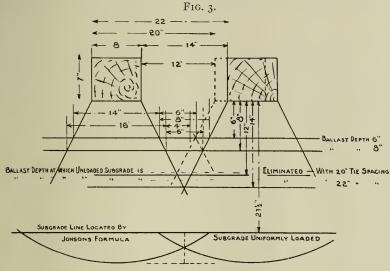
For gravel, 
$$d' = \frac{8}{3} (S - \frac{3}{4}b')$$
  
For stone,  $d' = \frac{4}{3} (S - \frac{3}{4}b')$ 

both of which give values of d' much greater than exist in practice.

The question whether, in order to strengthen our tracks for the increased loads imposed, the number of ties or the depth of ballast, or both, should be increased, is one upon which opinions vary widely among those concerned. The following is here presented in this connection:

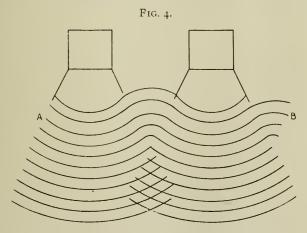
Fig. 3 shows a diagrammatic section of the ordinary standard main line track, in which 7-inch by 8-inch ties are spaced 22 inches apart, or 18 per 33-foot rail, and laid upon 6 inches of ballast. The slopes of the ballast pyramids, transmitting the load from bottom of tie to subgrade, are determined in accordance with Mr. Johnson's premises for the distribution of pressure at the bottom of stone ballast. It will be noted that the width of the base of the ballast pyramid under each tie is 14 inches and the width of the strip of subgrade unloaded and lying between adjacent ties is 8 inches. As shown by Director Schubert's experiments, and in line with the experience of all trackmen, the subgrade line, originally straight, will be disturbed, as AB in

Fig. 4, the amount of disturbance being proportional to the weakness of the subgrade and to the ratio of the area of subgrade



Section of Standard main line track.

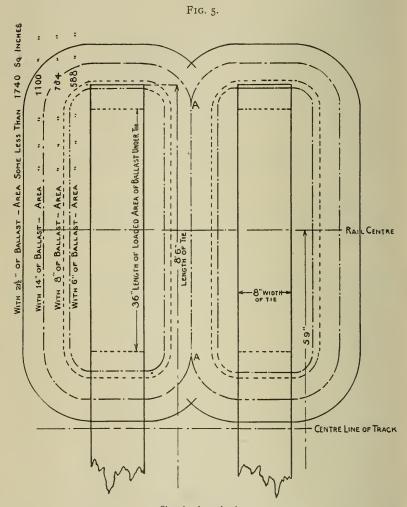
between the loaded ballast pyramids and that of subgrade beneath the ballast through which the load is transmitted.



Sketch showing distortion of ballast under loaded ties.

By changing the tie-spacing to 20 inches, or 20 per 33-foot rail, as shown dotted in Fig. 3, the ratio of loaded to unloaded

width of subgrade at the 6-inch depth of ballast becomes 14/6 instead of 14/8, an increase of 33½ per cent. The subgrade is more nearly confined, a condition which, of course, materially



Sketch of track plan.
7" x 8" x 8' 6" ties spaced; 22" or 18" per 33' rail. Showing outlines and areas of loaded sections of subgrade with 6", 8", 14" and 21½" of ballast under the ties.

increases its carrying capacity. Maintaining the 22-inch tiespacing and increasing the depth of ballast from 6 inches to 8 inches changes the ratio of loaded to unloaded width of sub-

grade from 14/8 to 16/6, an increase of approximately  $52\frac{1}{2}$  per cent.; while the combination of the decreased tie-spacing and increased ballast depth increases the original ratio from 14/8 to 16/4, or approximately 128.6 per cent.

In the diagrammatic plan of track shown in Fig. 5 it is assumed that the rail load is spread by the tie 18 inches on each side of the rail centres, or, for an 8-inch tie, over an area of 36 times 8 = 288 square inches of the lower face of the tie under each rail, and over somewhat less than the 36 + 6 times 8 + 6, or 588 square inches of the subgrade. The corresponding area of unloaded subgrade is 42 times 8, or 336 square inches, and the ratio of loaded to unloaded subgrade areas is 588/336. Decreasing the tie-spacing to 20 inches will increase this ratio to 558/252, or  $33\frac{1}{3}$  per cent., while combining with this decrease, an increase of ballast depth of 2 inches, will increase the ratio to 588/168, or 100 per cent.

Fig. 5 also shows that with 18 ties per 33-foot rail the unloaded area of subgrade between adjacent ties becomes zero when the depth of ballast is increased from 6 inches to 14 inches, while with 20 ties per 33-foot rail it becomes zero with a ballast depth of 12 inches.

According to Johnson's formula for stone ballast, uniform distribution of subgrade loading will be obtained with 21½ inches of ballast for 18 ties per 33-foot rail and with 18½ inches of ballast for 20 ties per 33-foot rail.

Any consideration of the relief to be expected from decreasing the tie-spacing, increasing the depth of ballast or otherwise, should take into account the cost, and in this connection Table II is presented on page 214.

From this table it is seen that a reduction of tie-spacing from 22 inches to 20 inches increases the ratio of width of loaded to unloaded subgrade by 33½ per cent. at a cost of \$464, \$928, and \$1856 per mile for single, double, and four-track lines respectively, while an increase of ballast depth of two inches (from 6 inches to 8 inches) increases this ratio by 52½ per cent. at the respective cost of \$256.90, \$507.23, and \$1006.51 per inch additional ballast, or \$513.80, \$1014.46, and \$2013.02 for the two inches of additional ballast. Whether the first or the second or a combination of both is best is therefore somewhat of an open question.

Some individuals and committees have recently recommended a ballast depth greatly in excess of previously existing standards and still greater than the ballast depths actually obtaining even on our densely travelled lines, without qualification dependent upon either the subgrades or the characteristics of the imposed loads.

#### TABLE II.

STATEMENT SHOWING COMPARATIVE COST OF INCREASING NUMBER OF TIES PER RAIL LENGTH (33 FEET) FROM 18 TO 20 AND COST PER INCH DEPTH OF PUTTING ADDITIONAL BALLAST UNDER STANDARD TRACK OF ONE OF OUR LARGER LINES.

Single

Double-

Ties per mile spaced	track	track	4-track
18 per rail length	2,880	5,760	11,520
20 per rail length	3,200	6,400	12,800
Additional ties	320	640	1,280
8 spikes	Cost of back Cost of la yard.	allast, <b>75 cent</b> aying ballast, t of ballast i	bic feet. s per cubic yard. 40 cents per cubi n track, \$1.15 pe
Credit account ballast displaced			
Net cost per tie\$1.15 Labor, placing tie in track30			
Cost per tie in track\$1.45 Cost of additional ties in track	\$464*	\$928*	\$1,856*
Full width of ballast base Cubic yards per square inch section per mile equals 1.35	164½"	324½"	644½''
Cubic yards ballast required Cost of required ballast in track, at	223.39	441.07	875.23
\$1.15	\$256.9	\$507.23	\$1006.51

<sup>\*</sup>Does not include labor cost of respacing present ties to make the insertion of additional ties possible, nor the cost of distributing the ties and ballast to point where placed in track.

To the writer it appears that the design of railroad track must be approached in the same way as the design of any mechanical parts. As a foundation it should be treated like any other foundation, and a study of its requirements, purposes, construction, and maintenance should be made. It must be designed to carry loads of certain individual magnitude, density and speed, etc., and must do this upon subgrade of given condi-

tions. With a sufficient amount of the right kind of data, it should be possible to combine the knowledge of the loads to be imposed with that of the subgrade conditions, and prescribe the most efficient and economical track construction, which, if it cannot be immediately provided, can be approached from year to year in connection with regular track maintenance work. Subgrade conditions vary materially within short distances, but with these conditions properly charted it should be a very easy matter, in bringing the condition of the track up to a desired standard, to concentrate effort upon those sections which are farthest from that standard and which will be located from tabulated or charted data or from the frequency of service failure.

Opinions of maintenance men vary greatly upon a majority of questions relating to track and track superstructure design, and practically none of these opinions is supported by such conclusive test or experience as will make early agreement or reconciliation possible. In the maintenance-of-way department dependable data are not being collected as in the motive power department, in which department much money has been, and is continually being, profitably spent to settle questions pertaining to the design and operation of both locomotives and cars, many of which questions are of less importance than some of those relating to track construction.

The writers upon maintenance-of-way subjects will have served a useful purpose if they succeed in focusing attention upon the comparative deficiency of experimental work in this field, for as soon as this deficiency is realized then work will be inaugurated which will, in a few years, elevate the science of track construction to its proper level. The condition of our tracks is now lagging behind requirements, and we cannot consistently hope for a better state of affairs unless some move along scientific lines is soon inaugurated. In the meantime, locomotive and car designers must "mark time," so far as increased loads and speeds are concerned.

While some investigations should necessarily be made under regular service, many can, nevertheless, be (and a few have been) carried out upon an experimental track of significant proportions. An experimental track was constructed a comparatively short time ago by the Prussian State Railroads at Oranienburg, Germany, and is being used to determine experimentally

the best construction. Dr. H. K. Hatt, of Purdue University, who visited this installation a few years ago, reported:

"It consists of an oval track two miles in circumference over which runs a train consisting of electric locomotive and cars. At about every fifty feet two vertical rail ends were sunk in the ground on each side of the track and clips riveted onto them to serve as a reference line, for measurement of track deformation. The service is considered as severe in one year as eight years on the main line. The cost of the roadbed and equipment is stated to have been \$40,000.

"About a year before my visit the first track had become worn out and a new track consisting mainly of steel and beech ties had been set under service.

"Some of the elements which were being experimented with at Oranienburg may be listed as follows: Prussian standard steel ties with side ribs have been down one year in different forms of ballast. The evidences of derailment of cars were visible, but the steel ties were not sprung. The modern double steel tie was used at the joints.

"Various forms of anchorage of rails to ties were under experimentation. These anchors are found more necessary in steel ties than in the case of wood. The various forms of anchors seemed all to be effective, although the track as a whole had not been down long enough to give final results.

"The scarf joint appeared to be unsuccessful, inasmuch as the inner edge of the scarf sheared off at the edge, due to the wave motion in the rail.

"The records of traffic passing over this experimental track show that in 369 working days the number of kilometre tons was about six million. In the months of January, February, March, and April, in 1909, there were nearly seven million kilometre tons. The locomotive weighed 59½ tons and would pull a train of from 240 to 375 tons. The speed of the train was 60 kilometres per hour.

"At the time of my visit the plant was not in operation.

"The above notes were jotted down from conversation with one of the officials in charge at the time of the visit, and were not submitted to the railway authorities for confirmation. They should serve, therefore, to illustrate the programme of work rather than to present official conclusions." The loads imposed upon this experimental track are insignificant in comparison with those which, for the results obtained to be of service, would have to be placed upon such a track in this country.

The writer would suggest that an experimental track be designed and constructed in the form of a figure 8, so that one loop could be operated while the other was being prepared for test. On this track, properly enclosed by fencing, etc., a motor, hauling any desired combination of cars, loaded with any desired axle loads, could be controlled from the office of an engineer of maintenance-of-way tests located in the centre of either of the loops, and in this way any combination of rails, fastenings, ties, joints, ballast, frogs, switches, signals, and safety devices could be tested.

The value of an ability, by this method, to rapidly test rails of different steels, under more scientific conditions, must be apparent when the amount of work done in settling rail questions during the last ten years is considered.

Such a plant, with its so general benefits, could be very properly be jointly constructed by interested railroads, perhaps under the direction of the American Railway Engineering Association, and tests on it carried out by some one of our educational institutions interested, in much the same way that motive-power department tests of various equipment furnished by different railroads, directly or indirectly through the Master Car Builders and Master Mechanics' Association, have for some years been conducted at Purdue University, Lafayette, Ind.

Panama-Pacific International Exposition, San Francisco, February 20-December 4, 1915.—The Department of Liberal Arts, of which Theodore Hardee has recently been appointed chief, announces that special efforts will be made to obtain a complete collection of exhibits of architecture, its allied arts and engineering. It will comprise drawings, models, and photographs of architecture and engineering in their various branches; plans followed in the improvement of rivers and harbors, water-works and sanitation; irrigation and roadmaking methods; specimens of artificial stone and kindred building material; processes used in testing structural materials, and special contrivances for safety, comfort and convenience in buildings. Detailed information may be had by addressing the Exposition.

Vol. CLXXVI, No. 1052-16

Influence of the Metalloids on the Properties of Cast Iron. H. I. Coe. (Iron and Steel Inst., May, 1913.)—American washed iron was melted under charcoal in a graphite crucible, and when melted suitable alloys of the metalloids were added to form a series of 54 alloys, containing carbon 3.0, silicon from 0.4 to 2.24, manganese from 0.14 to 2.22, sulphur 0.11 to 0.45, phosphorus 0.30 to 2.88 per cent. Transverse strength, deflection, tensile, and hardness tests were made and the results tabulated. The conclusions are: (1) Silicon decreases the strength and hardness of cast iron, owing to its effect in promoting the decomposition of iron carbide. (2) Manganese to the extent of 0.5 per cent. softens silicious gray irons, owing to its effect on the condition of the carbon; the strength is increased by the addition of manganese. (3) The influence of sulphur is largely determined by the silicon present. controlled, it should be of considerable value to the iron founder in mixing his iron for any particular purpose. (4) In the absence of manganese, and with about 2 per cent, silicon present, very strong gray irons may be obtained if the percentage of sulphur be judiciously raised. (5) Phosphorus, up to about I per cent., is useful. It confers fluidity, slightly increases the strength, and also slightly diminishes the hardness of the metal. A higher percentage gives a hard brittle material. The influence of the metalloids on the pearlite formation was also investigated, and the cooling curves of six phosphoric irons are given. The paper includes nine microphotographs.

A New Use for Metallic Cobalt. Anon. (Brass World, ix, 6, 217.)—From an article in the Ironmonger it appears that cobalt may be largely used in steel manufacture. Steel experts in Sheffield are experimenting with a new grade of high-speed steel which contains a small proportion of cobalt in addition to tungsten, vanadium, and other usual ingredients. The effect of cobalt is to intensify the characteristic qualities of tungsten and vanadium and to impart to the tools increased speed and durability. Cobalt steel is already made in America and Germany, and some is offered in England at very high prices. The Sheffield steel makers will not offer this new steel to the engineering world till experiment has demonstrated beyoud doubt its permanent commercial value, and the particular purposes for which it is adapted. A small quantity has been made in Sheffield, and some manufacturers have been asked to supply it. Cobalt is found in Ontario, and at present the supply is limited, but there is plenty of ore which could be mined if a regular demand arose. The current price is \$2500 to \$3000 per ton. Cobalt steel will be more expensive than the best vanadium steels, and it is not thought in Sheffield that it will supersede the present high-speed steels to any considerable extent, although it will be advantageous for various purposes. Experiments as to the effect of cobalt on carbon steel mixtures are being made.

## NOTES FROM THE U.S. BUREAU OF STANDARDS.\*

#### A CONVENIENT SECONDARY STANDARD OF RADIATION.

Pending preparation of the full announcement, a preliminary note upon the secondary standard of radiation of the Bureau may prove of interest.

There has been heretofore no convenient standard of radiation analogous to the photometric standard now maintained at the national standardization laboratories. In order to attain a greater uniformity in rating its own radiometric work, and with the hope of placing radiometric work throughout the country upon a uniform basis, the Bureau of Standards has undertaken to maintain such a standard of radiation.

This is a secondary standard, in the form of well-seasoned carbon filament incandescent lamps, rated to give in absolute units the energy per square centimetre at a distance of I metre. The primary standard is the radiation from a uniformly-heated inclosure, the so-called black body. The coefficient of radiation (the Stefan-Boltzmann constant,  $\sigma$ , in the formula,  $E = \sigma T$ . where E = energy per square centimetre and T is absolute temperature Centigrade) is taken to be  $\sigma = 5.7 \times 10^{-12}$  watt, or  $1.36 \times 10^{-12}$  gramme calorie per second. This value for the coefficient is based upon the most recent measurements, and may be modified in future years when more accurate determinations become possible. In the meantime it will be an advantage for all experimenters to work on the same basis, even though that basis may be I to 2 per cent. in doubt. This will be more satisfactory than the only simple basis of comparison now at hand, viz., the Hefner flame standard. Angström found the radiation at I metre from the Hefner lamp (through a diaphragm having an opening 14 by 40 mm. placed 10 cm. from the flame) to be  $S = 21.5 \times 10^{-6}$  gramme calorie per square centimetre; while a direct comparison with a black body, at the Bureau of Standards, gave  $S = 23.4 \times 10^{-6}$  gramme calorie per square centimetre, when using a diaphragm having an opening of 14 by 40 to 14 by 43 mm. When the opening was 14 by 50 mm, the value

<sup>\*</sup> Communicated by the Bureau.

was  $S = 24.7 \times 10^{-6}$ , and when no diaphragm was used the value was  $S = 26.8 \times 10^{-6}$  gramme calorie per square centimetre.

The transfer from the primary to the secondary radiation standard,—i.e., the comparison of the incandescent lamps with the black body,—was made by means of several of the Bureau of Standards form of bismuth-silver thermopile. The experimental error in the measurements on the incandescent lamps was of the order of 0.8 per cent. These measurements were made in the summer time, when there is greater temperature uniformity, permitting the operation of a thermopile in open air. In the autumn and winter it is usually quite impossible to operate delicate radiometers which are open to the air. Hence provision has been made for giving the value of the radiation from the standard lamp when the radiometer is covered with a glass window to avoid air currents.

If desired, the incandescent lamps can be rated both for candle-power and radiation, thus giving a standard of light and

of radiation in one lamp.

In various investigations of photo-synthesis, of photo-electric phenomena, and in psychological problems, the intensity of the stimulus should be measured radiometrically by means of some simple radiometer.—e.g., a thermopile with its auxiliary galvanometer. Knowing the area of the receiving surface exposed to the stimulus, the value of the stimulus in absolute units may be determined at once by exposing the thermopile to the standard of radiation. In this manner it will be possible to make more accurate and more uniform measurements of the stimuli acting in these various phenomena than have yet been obtained.

#### TESTING POTENTIAL TRANSFORMERS.

By H. B. Brooks, Bureau of Standards.

The commercial importance of instrument transformers has stimulated the development of accurate methods for the determination of their ratio and phase angle. These methods are suitable for the laboratory only. A method is wanted which, while giving all needed accuracy, can be carried out at the point

of installation, using commercial instruments and the ordinary supply voltage. Such a method of testing potential transformers is described in the present appear.

is described in the present paper.

The primary windings of a standard transformer and the transformer to be tested are connected to the same supply. The secondary windings are connected in series so that their voltages are opposed. The small difference between the two secondary voltages is measured by means of an indicating wattmeter whose current coil is separately excited by a current in phase with the supply voltage. The ratio of transformation of the transformer under test may then be readily calculated.

By making the above test with the primaries connected to a two-phase circuit, a measurement of the difference of the phase angles of the two transformers may be made by exciting the current coil of the wattmeter from the second phase. If a two-phase circuit is not available, the test for phase angle may be made by exciting the wattmeter current coil from another phase of a three-phase circuit, and applying a simple correction factor.

A comparison of the above method and a standard laboratory method gave values for ratio agreeing to less than 0.1 per cent., and of phase angle within one minute.

## A COMPARATIVE STUDY OF AMERICAN DIRECT-CURRENT WATTHOURMETERS.\*

By T. T. Fitch, Bureau of Standards.

This paper gives the results of numerous tests on six makes of American watthourmeters. The discussion is given under three headings: Performance Data; Details of Construction; Effect of Friction Losses.

Performance Data.—The load curve is shown to be a curve, which for the ordinary adjustment of the meter being correct at 10 per cent. and full load results in the meter being fast between 10 per cent. and full load and slow at over loads. The meters showed a variation of from 1 to 8 per cent. for a variation of voltage from 84 to 116 per cent. of the normal. For

<sup>\*</sup> Scientific paper to appear in the Bulletin of the Bureau of Standards, vol. 10.

three-wire meters the two current elements were found to differ from equality by from 0.4 to 4.0 per cent. The range of starting coil adjustment at 10 per cent. load varied from 4 to 22 per cent. in rate of the meter for the different makers. The range of the magnet adjustment varied from 35 to 155 per cent. in change of the meter rate for the different makers. The meters were affected by short circuit on 220 volts, as shown by changes in the rate of from 0 to 34 per cent. The back electromotive force in the commutator meters at full load ranged from .07 to .19 volt and was about —0.1 per cent. per degree C., except for one meter which gave 0.25 per cent.

Effect of Friction Losses.—The friction torques due to the bearings, the brushes, the gearing, and the air were measured. The friction torques, with the exception of the air friction torque, are curvilinear functions of the speed.

Finally the load curve of the commutator meter is analyzed and its curvature shown to depend on the back electromotive force, the variation in the friction torque, and the change in rate caused by heating of the series coils. The discussion has not been extended to the mercury type meter in as complete form.

Influence of Sulphur on the Stability of Iron Carbide. W. H. HATFIELD. (Iron and Steel Inst., May, 1913.)—An investigation in which three series of steels were employed, containing carbon 2.85 to 3.2 per cent., silicon 0.29 to 1.09, sulphur 0.01 to 0.85, and manganese 0.0 to 0.18 per cent., led to the conclusion that sulphur increases the stability of iron carbide, the action being chemical, not mechanical, as Levy suggested, and probably effected by a small percentage of sulphur associated with the carbide crystals; yet the action of sulphur is neutralized by manganese and also to a large extent by silicon.

A New Process for Coating Metals with Tin or Lead. Anon. (Brass World, ix, 6, 219.)—This patent was taken by Fritz Plathner and Nictor Dorn, of Berlin. For tinning, clean the metal from rust, scale, or grease, then mix two pounds tin powder and one pound zinc chloride to a paste with water or alcohol and spread over the metal. Then heat until the tin melts, and the whole surface will be covered with an adherent layer of tin. For coating with lead use the same method, only substituting powdered lead for tin. Ammonium chloride may be used instead of zinc chloride. Tin and lead powders are now commercial articles.

## THE FRANKLIN INSTITUTE

#### MEMBERSHIP NOTES.

#### Elections to Membership.

(Stated Meeting of the Board of Managers, July 9, 1913.)

#### RESIDENT.

Dr. Gellert Alleman, Department of Chemistry, Swarthmore College, Swarthmore, Pa.

Mr. W. Bancroft, Lanston Monotype Machine Co., Philadelphia, Pa.

Mr. W. C. CARNELL, 2136 North Camac Street, Philadelphia, Pa.

Mr. Samuel F. Houston, 509 Real Estate Trust Building. Philadelphia, Pa.

Mr. R. A. F. Penrose, Jr., 460 Bullitt Building, Philadelphia, Pa.

Mr. Joseph Rosin, 715 Green Street, Philadelphia, Pa.

#### NON-RESIDENT.

Dr. Carl L. Alsberg, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

DR. EDWARD BARTOW, Director, State Water Survey, Urbana, Ill.

Mr. Lucius P. Brown, Nashville, Tenn.

Dr. E. W. CALDWELL, 480 Park Avenue, New York, N. Y.

Dr. Charles A. Doremus, 55 West Fifty-third Street, New York, N. Y.

PROF. W. L. DUDLEY, Vanderbilt University, Nashville, Tenn.

MR. W. H. ERHART, Charles Pfizer & Co., 81 Maiden Lane, New York, N. Y.

Mr. Dudley Farrand, Newark, N. J.

Mr. T. T. Greenwood, 677 Western Avenue, Lynn, Mass.

Mr. Jacob Hasslacher, 100 William Street, New York, N. Y.

Mr. I. P. LIHME, The Grasselli Chemical Company, Cleveland, Ohio.

Mr. Arthur D. Little, President, A. D. Little, Inc., Boston, Mass.

MR. JOHN URIC LLOYD, Lloyd Brothers, Court and Plum Streets, Cincinnati, Ohio.

MR. E. MALLINCKRODT, JR., Mallinckrodt Chemical Works, St. Louis, Mo.

Prof. W. Lash Miller, 50 St. Alban Street, Toronto, Canada.

PROF. EDWARD W. MORLEY, West Hartford, Conn.

Mr. B. L. Murray, Merck & Company, Rahway, N. J.

Mr. Thomas E. Murray, 57 Duane Street, New York, N. Y.

Dr. Wm. H. Nichols, 25 Broad Street, New York, N. Y.

Dr. Julius Stieglitz, University of Chicago, Chicago, Ill.

PROF. CHARLES D. TEST, Colorado School of Mines, Golden, Col.

Dr. L. M. Tolman, Chief, Food Inspection Bureau, U. S. Department of Agriculture, Washington, D. C.

Mr. Orville Wright, President, The Wright Company, Dayton, Ohio.

#### Changes of Address.

Mr. Walter Atlee, 3044 N Street, N. W., Washington, D. C.

Mr. C. W. Barwis, 529 Pennsylvania Avenue, Elmira, N. Y.

Mr. Charles H. Davis, South Yarmouth, Mass.

Mr. C. D. Ehret, 6911 Clearview Street, Mt. Airy, Philadelphia, Pa.

Mr. F. Winsor Eveland, Westinghouse, Church, Kerr & Co., 37 Wall Street, New York, N. Y.

Mr. F. H. GILPIN, 3101 Passyunk Avenue, Philadelphia, Pa.

Dr. Joseph S. Hepburn, Food Research Laboratory, 1833 Chestnut Street, Philadelphia, Pa.

Mr. Henry Hess, 928 Witherspoon Building, Philadelphia, Pa.

MR. ANDREW W. HILL, Linden Avenue, Laurel Springs, N. J.

Mr. Conrad Lauer, 611 Chestnut Street, Philadelphia, Pa.

Mr. RICHARD WALN MEIRS, Rooms 226–227 Weightman Building, 1524 Chestnut Street, Philadelphia, Pa.

Mr. Eugene Merz, The Heller & Merz Company, Hamburg Place, Newark, N. J.

MR. C. E. SARGENT, 2272 North Meridian Street, Indianapolis, Ind.

DR. WM. O. SMITH, 1509 Arch Street, Philadelphia, Pa.

Mr. Frank H. Stewart, 37 and 39 North Seventh Street, Philadelphia, Pa.

MR. G. A. Wells, 17 Darling Avenue, Mount' Vernon, N. Y.

#### THE RAILWAY TUNNELS OF NEW YORK CITY.

BY

## ALFRED NOBLE, C.E., LL.D.

#### A CORRECTION.

Vol. CLXXV, page 383, line 7 from bottom, for "Hudson" read "Harlem."

' 384, in table, for "5166" read "5375;" for "6676" read "6994;" for "9102" read "9431."

#### LIBRARY NOTES.

#### Purchases.

Askling, C. W., and E. Roesler,—Internal Combustion Engines and Gas Products. 1912.

Collignon, E.—Cours de mécanique appliquée aux constructions. Third edition. 2 vols., 1880, 1885.

Electrical Trades Directory and Handbook for 1913.

Festschrift W. Nernst zu seinem fünfundzwanzigjährigen Doktorjubiläum gewidmet von seinen Schülern. 1912.

GESCHWIND, L.—The Manufacture of Alum. 1901.

Houstown, R. A.—An Introduction to Mathematical Physics. 1912.

McNicol, D.-American Telegraph Practice. 1913.

Newell, F. H., and D. W. Murphy.—Principles of Irrigation Engineering. 1913.

PATCHELL, W. H.—Applications of Electric Power to Mines. 1913.

REGNAULT, V.—Relation des expériences des machines à vapeur. 4 vols. 1847, 1862, 1870,

SELLEW, W. H.-Steel Rails. 1913.

TAYLOR, F. W .-- On the Art of Cutting Metals. 3d edition. No date.

THORKELSON, H. J.—Air Compression and Transmission. 1913.

Watson, W.-Advanced Textile Design. 1913.

#### Gifts.

- Baldwin Locomotive Works, The, Record Nos. 73 and 74. Philadelphia, 1912 and 1913. (From the Works.)
- Baylor University, Catalogue 1912–1913. Waco, Tex., 1913. (From the University.)
- Canada Board of Railroad Commissioners, Seventh Report, March 31, 1912. Ottawa, 1913. (From the Commissioners.)
- Canada Department of Mines: Annual Report on the Mineral Production of Canada for 1911. The Magnetic Iron Sands of Natashkwan. Ottawa, 1912 and 1913. (From the Department.)
- Canada Department of Trade and Commerce, Report for 1912, Part 7. Ottawa, 1913. (From the Department.)
- Carnegie Endowment for International Peace, Year Book for 1912. Washington, D. C., 1913. (From the Endowment.)
- City and Guilds of London Institute, Report of the Council, 1913. London, 1913. (From the Institute.)
- Columbia University: Publication No. 4 of the Ernest Kempton Adams Fund for Physical Research, Graphical Methods, by C. Rungl. Publication No. 6, Researches in Physical Optics, Part 1, by R. W. Wood. New York City, 1912 and 1913. (From the University.)
- Connecticut Agricultural Experiment Station, 26th Annual Report, 1912. Hartford, 1913. (From the Station.)
- Delaware College, Catalogue 1913. Newark, Del., 1913. (From the College.) George Washington University, Catalogue, March, 1913. Washington. D. C., 1913. (From the University.)
- Georgia Geological Survey, Bulletin No. 20, A Preliminary Report on the Mineral Springs of Georgia, by S. W. McCallie. Atlanta, 1913. (From the State Geologist.)
- Laws of Vermont, 1912. Montpelier, 1913. (From the State Librarian.)
- Nebraska State Railway Commission, Fifth Annual Report, 1912. Lincoln, 1912. (From the Commission.)

- New York State Department of Health, Report on the Application of Ozone to Water Purification, by R. Spaulding. Albany, 1913. (From the Department.)
- Société des Arts de Geneve, Comptes Rendus de l'exercice 1912. Geneva, Switzerland, no date. (From the Société.)
- South Australia Geological Survey, Bulletin No. 2, and Review of Mining Operations, No. 17. Adelaide, Australia, 1913. (From the Survey.)
- United States Commissioner of Education, Report for 1912. Vols. 1 and 2. Washington, D. C., 1913. (From the Bureau of Education.)
- U. S. Department of Commerce: U. S. Coast and Geodetic Survey—Determination of Time, Longitude, Latitude and Azimuth, by W. Bowie. 5th edition. Washington, D. C., 1913. (From the Department.)
- University of Arkansas, Catalogue 1912–1913. Fayetteville, Ark., 1913. (From the University.)
- University of Michigan, Calendar 1912-1913. Ann Arbor, 1913. (From the University.)
- University of Washington, Catalogue 1912-1913. Seattle, Wash., 1913. (From the University.)
- Yale University, Report of the President, 1912-1913. New Haven, 1913. (From the University.)

#### BOOK NOTICES.

Carnegie Institution of Washington, Publications.—The following volumes are announced for early publication:

- No. 173. REICHERT, EDWARD T.—The Differentiation and Specificity of Starches in Relation to Genera, Species, etc.: Stereochemistry Applied to Protoplasmic Processes and Products, and as a Strictly Scientific Basis for the Classification of Plants and Animals. Quarto, in two parts. Part I. The Starch-Substance and Starch-Grain. Pages i–xviii + 1–342, 102 plates containing 612 photomicrographs, charts A–J. Part II. The Differentiation and Specificity of Starches. Pages i–xviii + 343–900 and 400 charts.
- No. 180. Jones, Harry C., and Collaborators.—The Freezing-point Lowering, Conductivity and Viscosity of Solutions of Certain Electrolytes in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Glycerol, and in Mixtures of These Solvents with One Another. Octavo.
- No. 186. Barus, Carl.—The Diffusion of Gases through Liquids, and Allied Experiments. Octavo.
- No. 190. Jones, Harry C., and J. S. Guy.—Absorption Spectra of Solutions as Affected by Temperature and by Dilution: A Quantitative Study of Absorption by Means of the Radiomicrometer. Octavo.
- No. 192. HUNTINGTON, ELLSWORTH, with contributions by CHARLES SCHUCHERT, A. E. DOUGLAS, and C. J. KULLMER. The Climatic Factor as Illustrated in Arid America. Quarto.

CHRONOLOGY OF AVIATION, by Hudson Maxim and William J. Hammer, New York. Reprinted from the World's Almanac for 1911. 23 pages, 8vo.

The Institute has received from Mr. Hudson Maxim and Mr. William J. Hammer 200 copies of the reprints which they have just issued of their "Chronology of Aviation," originally prepared for the World's Almanac of 1911. The data embrace the essential facts relating to aerial progress. In addition to a short historical résumé, are given tables of altitude records, speed records, quick-starting and slow-speed records, passenger carrying. English Channel and other over-water flights, cross-country flights, notable distance and duration flights. There are statistics relating to accidents and data relative to spherical and dirigible balloons or airships, etc. Of special interest are the tables giving the most important flights of the Wright Brothers.

Copies may be had without charge on application to the Secretary of the Institute.

#### PUBLICATIONS RECEIVED.

North Carolina Geological and Economic Survey, Joseph Hyde Pratt, State Geologist: The Coastal Plain of North Carolina, by Wm. Bullock Clark; Benjamin L. Miller, L. W. Stephenson, B. L. Johnson, and Horatio N. Parker. 552 pages. Illustrations, plates, maps, tables, 4to. Raleigh. State Printers, 1912.

U. S. Commissioner of Education, Report for the year ended June 30, 1912. 2 volumes. 8vo. Washington, Government Printing Office, 1913.

U. S. Bureau of Standards: Technologic Paper No. 12—Action of the Salts in Alkali Water and Sea Water on Cements, by P. H. Bates, A. J. Phillips, and Rudolph J. Wig. [November 1, 1912.] 157 pages, illustrations, plates, 4to. Washington, Government Printing Office, 1913.

The Transit, 1913. Edited by the Associated Students of Applied Science of the State University of Iowa. 50 pages, illustrations, portrait, 8vo. Iowa City, University, 1913.

Iowa State College of Agriculture and Mechanic Arts: Bulletin No. 31, Engineering Experiment Station—The Theory of Loads on Pipes in Ditches and Tests of Cement and Clay Drain Tile and Sewer Pipe, by A. Marston and A. O. Anderson. 181 pages, illustrations, 8vo. Ames, College, 1913.

U. S. Office of Public Roads: Circular No. 99—Process Reports of Experiments in Dust Prevention and Road Preservation, 1912. 51 pages, 8vo. Washington, Government Printing Office. 1913.

U. S. Bureau of Mines: Bulletin 51—The Analysis of Black Powder and Dynamite, by Walter O. Snelling and C. G. Storm. 80 pages, illustrations, plates. 8vo. Bulletin 54—Foundry-cupola Gases and Temperatures, by A. W. Belden. 29 pages, illustrations, plates. 8vo. Technical Paper 37—Heavy Oil as Fuel for Internal-combustion Engines, by Irving C. Allen. 36 pages, 8vo. Monthly Statement of Coal-mine Fatalities in the United States, April, 1913, with revised figures for preceding months, compiled by Albert H. Fay. 15 pages, 8vo. Washington, Government Printing Office, 1913.

Iowa State College of Agriculture and Mechanic Arts: Bulletin No. 30, Engineering Experiment Station—The Determination of Internal Temperature Range in Concrete Arch Bridges, by C. S. Nichols and C. B. McCullough. 101 pages, illustrations, plates, 8vo. Ames, College, 1913.

University of Wisconsin: Bulletin No. 529—Theory and Test of an Overshot Water-wheel, by Carl Robert Weidner. 136 pages, illustrations,

plates, 8o. Madison, University, 1913.

Ignition of Mine Gases by the Filaments of Incandescent Lamps. H. H. CLARK and L. C. ILSLEY. (U. S. Bureau of Mines Bull. lii, 1913.)—Most of the experiments were made with a mixture of 91.4 per cent. of air and 8.6 per cent. of natural gas containing CH<sub>4</sub> (methane) 82, C<sub>2</sub>H<sub>6</sub> (ethane) 16.4, N<sub>2</sub> (nitrogen) 1.5, and a trace of CO2 (carbon dioxide). Tests were made with 1219 standard lamps and 234 miniature lamps. The naked filaments of all standard lamps, operated at rated voltage, will ignite the gaseous mixture used. All classes of standard carbon lamps will sometimes ignite the gas when the tips of the bulbs are broken off. The filament temperature of all classes of standard lamps, and of all but one class of miniature lamps, can be increased to such a degree that the lamps, when smashed, will ignite gas. When the bulbs of lamps burning at rated voltage were smashed, the results showed that 55and 100-volt lamps of all candle-powers ignited gas under the conditions of the tests, and that 32- and 50-candle-power 55-volt lamps invariably ignited gas. The 8-candle-power 220-volt lamps gave no ignitions, and, in general, the percentage of ignitions obtained from lamps of given candle-power decreased as the voltage increased. When the tips of bulbs were broken the percentage of ignitions increased as the candle-power rating increased, and decreased as the voltage rating increased. Although no class of lamps gave 100 per cent. ignitions, all classes caused some ignitions.

Prize Offered by the German Bromine Convention. Anon. (Chem. and Drug., May 17, 1913.)—A prize of \$2500 is offered by the German Bromine Convention to the discoverer of a process or compound which will lead to a new and increased consumption of bromine. The existing German bromine factories have produced far more bromine than has been consumed, so a fresh field of use is urgently needed. Some of the conditions of the competition are as follows: The new discovery must represent a technical innovation, and must not adversely affect existing uses of bromine. The process must be practically applied within one year, at the latest, after the award of the prize. In the opinion of the jury, the process must lead to a considerable increase in the European consumption of bromine at a suitable price. Competitors must send in their processes not later than January 1, 1914, to the Deutsche Bromkonvention G. m. b. H., Leopoldshall-Stassfurt.

## CURRENT TOPICS

Mortars and Concretes Mixed with Asphaltic Oils. A. TAYLOR and T. SANBORN. (Proc. Amer. Soc. Civil Eng., XXXIX, 355.)—Page's statements concerning oil-mixed concrete were subjected to a thorough investigation, and the following conclusions were reached as regards asphaltic oils: (1) Oil-mixed concrete containing 5, 10, or 15 per cent. of oil is more permeable under pressures of 20 to 60 pounds per square inch than ordinary concrete, and oil-mixed mortar containing 10 per cent. of oil is more permeable than plain mortar under pressure of 10 to 20 pounds per square inch. (2) Oil-mixed mortars containing up to 25 per cent. of oil show slightly less absorption of water than plain mortar, except that with the most viscous oils the mortar becomes more absorptive, and absorption is not an index of the permeability. The absorption decreases with the increase in the quantity of oil. (3) Both the tensile and the crushing strengths of oil-mixed mortars are considerably less than those of plain mortars, the strengths decreasing with the increasing quantities of oil, and the progressive deterioration with increase of oil being more marked in the case of crushing than of tensile strengths. (4) The strength decreases with the viscosity of the oils, and with the most viscous oils it requires considerably more water to keep a mixture at the normal consistence than is required in the fluid oil mixtures. (5) The relative decrease in strength with increasing quantities of oil in mortars is less in 50 days than in 28 days.

Density of Aluminum. F. J. BISLEE. (Faraday Soc., May 7, 1913.)—The density of aluminum varies considerably, according to the previous treatment, and under certain conditions the density of the cast metal may exceed that of the worked metal, though the density of the worked metal increases again on annealing. The worked metal etched with hydrofluoric acid shows under the microscope a structureless surface, with flow lines in the direction of the work. Cast aluminum under similar conditions is very distinctly crystalline.

Moulding Aluminum Alloys. Anon. (Brass World, ix, 5, 168.)—For all aluminum alloys, both the light alloys in which aluminum is the chief constituent or aluminum bronzes, the moulding sand must be worked as dry as possible. Wet sand causes the metal to boil and thus produces dross. It is unnecessary to skin dry the mould, but the sand should be as dry as it can be worked and not rammed too hard.

Influence of Incombustible Dusts on the Inflammation of Gaseous Mixtures. Anon. (Third Report of the Explosions in Mines Committee, March 11, 1913.)—A detailed account of an investigation conducted mainly with the object of testing the accuracy of Abel's conclusions regarding the supposed action of incombustible dusts in promoting the inflammation of non-inflammable mixtures of fire-damp and air. Exception is taken to Abel's statement that flame can be propagated in a current of air containing as little as 3.5 per cent. of fire-damp and having a velocity of 200 feet per minute, or more, since the combustible portion of the fire-damp used in Abel's experiments was practically all methane, and the lower limit of inflammation of this gas when admixed with air is 5.6 per cent. according to Burgess and Wheeler, and between 5.0 and 6.7 per cent. according to all other experimenters. Abel's results were probably due to incomplete mixing of the fire-damp and air, for with apparatus adapted to produce "streaky" gaseous mixtures results similar to those recorded by Abel—but, it is suggested, misinterpreted by him-were obtained. By repeating Abel's experiments under the same conditions he employed, but with well-mixed gases, and measuring the rapidity with which flame spread through the mixtures in the absence and in the presence of various dusts in suspension, it was found that the inflammability of mixtures below the lower limit of inflammation, or of explosive mixtures, travelling at different rates, was decreased when an incombustible stone or calcined magnesia dust was present. This conclusion was confirmed by further experiments made in a horizontal iron gallery, in a vertical glass tube, and in a spherical explosion vessel. Incombustible dusts tend to decrease, rather than increase, the inflammability of gaseous mixtures containing them.

Acetin. Editor. (Metal Industry, xi, No. 5, 215.)—Acetin is a compound made by slowly boiling two parts glycerine and one part acetic acid for 20 minutes, allow to cool, and bottle. It is used with good results on old oil paintings that show a tendency to crack or curl. It is also used to remove the yellow stain from old celluloid piano keys or other celluloid articles.

Experimental Determination of the Regulation of Alternators. A. B. Field. (Amer. Inst. Elect. Engin. Proc., xxxii, 599.)—The method of determining the regulation of an alternator from test results, which is incorporated in the Standardization Rules, is not accurate for low power-factors, as it fails to include the varying pole leakage or the ratio of armature reaction to reactive voltage drop. The effects of these are most marked at power-factor zero, and, as this is also the only power-factor at which a load regulation curve can usually be experimentally determined satisfactorily, it is advocated to base regulation determinations upon the power-factor zero load saturation and the no-load saturation.

Rock Salt in British Columbia. Anon. (Oil, Paint and Drug Rep., May 19, 1913.)—An extensive bed of rock salt has been discovered on the Skeena River, about 45 miles from Prince Rupert. Five holes have been drilled, about a mile apart, and salt has been struck in every case at depths varying from 50 to 250 feet. About 8 tons of salt have been raised. The product is absolutely pure and of the best quality.

Rust-proof Coating for Iron or Steel. Anon. (Amer. Mach., xxxviii, No. 18, 737.)—This new rust-proof coating is a paint that is applied to the surface of the article to be coated and is then baked. The ingredients are mixed in the following proportions: Linseed oil, 25 parts; calcium resinate, 36 parts; manganese borate, ½ part; lead acetate, 1 part; naphtha, 37½ parts; artificial graphite, 25 parts. These are mixed and applied to the metal by brushing, or dipping, or any other method. The article is then baked at 300° F. for 1 hour and 40 minutes. The coating is stated to be highly lustrous and resistant to corrosion. No other form of graphite gives satisfactory results.

Heat of Combustion of Diamond and Graphite. W. A. ROTH and H. WALLASCH. (Ber., xlvi, 896.)—Diamond and various species of graphite, both natural and artificial, were burned in a bomb calorimeter with paraffin oil to aid the combustion. For 1 gramme of diamond the figure 7869 calories was obtained, agreeing with that of Berthelot and Petit. The mean figure for graphite was 7854 calories per gramme, though some specimens gave only 7830 to 7835 calories. This difference cannot be explained. Blastfurnace graphite gave 7855 to 7865 calories, much lower than Berthelot and Petit's figure, 7907 to 7902. Even these figures become 7923 calories if more recent values for the heat of combustion of naphthalene be taken.

Potential Waves of Alternating-current Generators. W. J. Foster. (Amer. Inst. Elect. Engin. Proc., xxxii, 207.)—This article has a triple purpose: (1) To discuss briefly certain elements in design that affect the character of the potential wave. (2) To show the effect of load and operating conditions on the no-load wave. (3) To give illustrations of the potential waves—good, bad, and indifferent—of generators that actually supply the alternating-current systems throughout the country. There are ninety illustrations in all; a study of these, with the descriptions given, shows that the most perfect wave is obtained where the proper shading of the magnetic flux is attained either by shaping the poles, in the case of definite pole machines, or by the proper distribution of field winding in the case of cylindrical rotor machines, together with an irregular or more or less prime relation between the number of slots in the armature and number of poles.

Fuel Briquetting in the United States. E. W. PARKER. (U. S. Geol. Survey.)—The quantity of briquetted fuel made in the United States during 1912 at 19 plants was 220,064 short tons, valued at \$952,261, as compared with 218,443 tons, valued at \$808,721, in 1911. Seven of these plants used anthracite culm, 9 used bituminous or semi-bituminous slack, I used residue from gas manufactured from oil, I used anthracite culm and bituminous slack mixed, and I used peat. The best material for producing a smokeless product is anthracite culm, of which there is a plentiful supply in the anthracite region of Pennsylvania, and more is produced daily in the mining operations. It is hoped that in the near future the small sizes of anthracite that are now sold for raising steam, in competition with bituminous coal and at prices below the actual cost of production, will become more valuable as a raw material for the briquette manufacturer. The output of these small sizes from the breaking up of large coal exceeds 20,000,000 long tons annually, exclusive of 3,000,000 to 4,000,000 recovered annually from the culm banks by washeries. As briquetted fuel it should be worth \$3 to \$4 per ton. The cost of briquetting is \$1 to \$1.25 per ton.

Experience in European countries, and investigation at fueltesting plants of the Geological Survey in St. Louis, and the Bureau of Mines, Pittsburgh, have shown that lignites can be successfully briquetted without any binding material, and that the most satisfactory binders for anthracite, semi-anthracite, bituminous, and sub-bituminous coals are coal-tar pitch, gas-tar pitch, and asphaltic pitch, or inexpensive cementing mixtures that are practically water-

proof. Some manufacturers use no binder.

Porous Metals. R. Grimshaw. (Metal Ind., xi, No. 5, 203.) —Herr H. J. Hannover has made microscopic studies of the various metals which have revealed some curious facts in reference to their pores. When an alloy of 96 parts lead and 4 parts of antimony was heated nearly to the melting-point and then allowed to cool, at first small, growing crystals separated, but at a temperature of 442° F. the contents of the "passages" between these also "set." When the alloy was reheated, the contents of the "canals" were the first to melt, the rest becoming fluid by further increase of heat. In a hot furnace the contents of the spaces between the crystals could be separated by centrifugal force, so that a porous lead plate resulted. The first experiments yielded a lead plate with crevices, but when the lead plate was surrounded by an iron pocket, having one side of brass wire cloth through which the melted metal could be thrown, it was possible to produce several porous lead plates having millions of microscopically small pores in a few minutes. Calculation showed that the surfaces exposed were 50 times as great as before the centrifugalling process. The invention of this porous metal is especially interesting and important to the accumulator industry.

The Corrosion of Aluminum. G. H. BAILEY, D.Sc. (Eng., xcv, No. 2463, 374.)—After detailing numerous investigations on this subject, the following general conclusions are reached: (1) That, in general, the greater its degree of purity the less aluminum is acted upon by water and salt solutions. (2) That the corrosion is notably accentuated in presence of copper or sodium. (3) That where the percentage of silicon is higher than that of the iron the action is less pronounced in the case of water and acids, and more pronounced in salt solution. (4) That water and common salt solution, from which the air has been expelled, have no corrosive action. (5) That corrosion is accentuated (a) at high temperatures; (b) by the presence of impurities in the water, especially alkalies. (6) That unannealed metal is much more seriously corroded than annealed metal, doubtless owing to the unequal physical condition of the metal in the unannealed state. (7) That the results obtained by acting on aluminum with acids or alkalies afford no definite indication of its behavior in presence of water or aqueous solutions. Had it been possible to establish any parallel, the investigation of the corrosion of aluminum would have been much simplified, since the difficulties presented by the formation of suspended or adherent deposit would be eliminated.

Metallizing Siliceous Surface. Anon. (Metal Ind., xi, No. 5, 200.)—La Révue des Produits Chimiques gives a process for putting a metal coating on siliceous surfaces, such as glass, pottery, etc. This method consists in treating the surface, which must not be enamelled nor varnished, with a solution of silver fluoride, and then exposing it to a current of illuminating gas. Later the article is exposed to a temperature of 50° C., and at that temperature to a current of carbon bisulphide. This causes the deposition of finely-divided metallic silver on the non-conducting surface. This deposit

Thermal Electromotive Force of Tungsten and Molybdenum. E. F. Northrup. (Met. and Chem. Eng., xi, 45.)—Although tungsten and molybdenum oxidize at high temperatures, the author has been able to obtain the temperature-electromotive force curve of a thermo-couple composed of these two elements. In the experiments, temperatures were measured by the help of a platinum and platinum-rhodium thermo-couple. For the range o° to 1000° C. the electromotive force was found to be given in microvolts by  $E=4.61t-0.00436t^2$ , and when the cold junction is at o° C. the electromotive force is a maximum at 530° C. and is zero at 1060° C. In this range the current flows from tungsten to molybdenum at the hot junction. The author suggests that, if all samples are found to behave in the same way, the neutral point would be a convenient method of fixing the temperature, 1060° C.

Copper Production of the World. H. R. MERTON AND CO. (Mining and Eng. World, April 19, 1913.)—The output of copper in 1912 shows an increase of 15.2 per cent. over 1911. In spite of this the visible supplies in America and Europe decreased over 20,000 tons, indicating a consumption of approximately 1,024,500 tons, an increase of 11 per cent. over the previous year. The following table shows the production by countries in 1911 and 1912:

	1911.	1912.
Jnited States	483,865	554,835
Spain and Portugal	50,930	58,930
lussia	25,310	33,010
Boleo	12,165	12,450
Other parts of Mexico	48,740	58,395
apan	55,000	65,500
ustralia	41,840	47,020
anada	24,930	34,710
Chili	25,595	37,305
Aansfield	20,520	20,180
Miscellaneous	83,025	82,150
Total	871,920	1,004,485

Kukui Oil. E. V. WILCON. (Oil, Paint and Drug Rep., March 24, 1913.)—The nuts of the Kukui tree, which is found in several of the Oceanic Islands and also in parts of the West Indies, Brazil, and Florida, yield an oil, variously known as kukui oil, kekune oil, candlenut oil, walnut oil, and artists' oil. Probably about 15,000 acres in Hawaii are covered with the trees. If the nuts were systematically gathered an annual yield of about 2,375,000 gallons of oil should be obtained.

Granular Chromium as a Resistance Material for Electric Heating. O. Dony-Henault. (Comptes Rendus, clvi, 66.)—Granular chromium, tungsten, or molybdenum, etc., prepared by the thermite process, can be used for electrically heating crucibles, tubes, etc. The granules do not conduct at once; but they can, like coherers, be made conductors of electricity by passing a spark discharge in their neighborhood, or by coating them with Acheson's graphite, or by heating the metal with a Bunsen burner, when the current between the carbon electrodes at 110 volts will suddenly start; the graphite also seems to act by the heat generated in it by the current. To heat a crucible, a hollow is made in magnesia and filled with the granular metal, so that a layer of 2 to 4 mm. thick of metal surrounds the crucible; the current is introduced by carbon brushes and rings. Quartz tubes are jacketed with the metallic grains.

The "Pyro" Boiler-cleaning System. Anon. (Eng., xcv, No. 2463, 377.)—The difficulty of satisfactorily removing hard scale from the interior of steam boilers has induced the expenditure of much ingenuity and from time to time of large sums of money on the part of investors. These attempts met with more or less success, but, notwithstanding that, the old practice of hand-chipping with hammers is still usually adopted. The latest scientific method of removing scale has left the beaten track, and instead of applying scraping and percussion, as is usual, heat in a very intense form is utilized. The apparatus was brought out by Mr. Adolph Schror, and the process has been termed the "pyro" boiler-cleaning system. The plant required is extremely simple, consisting of an oxyacetylene blow-pipe with two or three jets, a portable acetylene generator, and a steel cylinder of compressed oxygen, together with the necessary length of flexible tubing. When any scale is to be removed, all that is necessary is to play upon it with the blow-pipe flame for a few minutes (time depends on the thickness of scale) until the scale cracks and falls off, due to the rapid expansion under the intense heat. The operation is easier if the scale is slightly damp. In an actual operation it has been found satisfactory. Care has to be taken to prevent the flame from playing on the bare plate for any length of time. When flat pieces of hard scale, some of them 5% inch thick, were held on the bare hand, with a piece of white paper between, and the flame was directed on the scale, this fell to pieces, while the paper was not scorched nor the hand burned. A distinct feature of the system is that it can be easily applied to almost inaccessible parts of a boiler, where hand-chipping is quite impossible. After cleaning off the scale the inside of the boilers is painted with "corrosanti" paint, which, it is claimed, prostresthe plates.

Decrease of Speed of Electrified Particles on Passing through Matter. N. Bohr. (Phil. Mag., xxv, 10.)—The theory of the decrease of velocity of moving particles in passing through matter is expressed in the form that the rate of the decrease depends on the frequency of vibration of the electrons in the atoms of the absorbing material. It is shown that the absorption of  $\alpha$ -rays in the lightest elements can be calculated from the information about the number and frequencies of the electrons in the atoms, which we get from the theory of dispersion, and that the values are in good agreement with experiment. For elements of higher atomic weight it is shown that the number and frequencies of the electrons we must assume, according to the theory, in order to explain the absorption of α-rays, are of the order of magnitude to be expected. It is further shown that the theory can account for the form of the relations between the velocity of the rays and the thickness of matter traversed, found by experiments with kathode-rays and β-rays. Adopting Rutherford's theory of the constitution of atoms,

it seems that it may be concluded with great certainty, from the absorption of a-rays, that a hydrogen atom contains only one electron outside the positively-charged nucleus, and that a helium atom contains two electrons outside the nucleus.

The Nature of Corona and the Dielectric Strength of Air. F. W. Peck, Jr. (Gen. Elect. Rev., xv, 781.)—A continuation of a previous work. It is shown first that the losses, established by calculation on the author's formulæ, agree with values actually measured on working lines, with special reference to Faccioli's and Hendricks' work. Then follows a section dealing with stroboscopic work, and the difference between the positive and negative halves of the alternating-current wave. The third section gives a theory explaining the apparent greater dielectric strength of air round small conductors as compared with that round larger conductors. The concluding paragraphs have reference to the limits which are likely to be set to high-voltage transmission by corona losses.

Molecular Phenomena not in Agreement with Thermodynamics. M. V. Smoluchoswski. (Phys. Zeitschr., xiii, 1069.) -The Brownian molecular motions, the opalescence of gases in the critical state, the blue of the sky, and some other phenomena have led to a decision in favor of a real kinetic theory of gases as distinct from the traditional purely phenomenalistic thermodynamics. The difference is most clearly brought out by a definition of the steady state. This used to be considered to be the state of minimum potential, to which an undisturbed body gradually approximates. The molecular kinetic view, on the other hand, admits the probability of continual fluctuations about this state, and of occasionally serious departure from it. The Brownian motions of particles denser than the containing liquid lead to a distribution according to a barometric exponential law, instead of a collection of all the particles at the bottom of the vessel. The work of Perrin on liquids and of Ehrenhaft and de Broglie on gases has fully confirmed this. The rule that the mean square of the concentration equals the reciprocal of the molecules contained in it has been successfully applied by Svedberg to gamboge emulsions and colloidal gold solutions. It is shown, too, that opalescence is due to the fluctuations in density of a gas.

Modifications of Iron below 700° C. F. ROBIN. (Rev. de Métallurgic, ix, 1083.)—A list is given of the points of singularity revealed in iron up to 700° C. A review of the evidence based on mechanical, magnetic, thermo-electric, and sonority tests made by numerous workers points to the existence of two allotropic changes in iron, one between 100° and 250° C. and the other between 400° and 500° C.

Aug., 1913.]

Monel Metal. R. H. GAINES. (Chem. News, cvii, 28.)—A synopsis is given of the methods of manufacture, the reduction having been so perfected as to give a product of very uniform composition, different analyses of different varieties only varying between the limits: Nickel, 67.55 to 69.54 per cent.; copper, 26.25 to 27.53 per cent.; carbon, 0.17 to 0.44 per cent., and iron, 2.07 to 3.33 per cent. In forged or rolled metal the manganese varies from 1.26 to 1.82 per cent., and the silicon from 0 to 0.37 per cent., while in cast metal the manganese varies from 0.09 to 0.49 per cent., and the silicon from 1.08 to 1.41 per cent. Variations in mechanical properties have little relation to variations in composition. Carbon appears to strengthen the alloy; iron hardens, whitens, and increases the strength, but appears to reduce the elastic limit. Silicon and manganese do not materially affect the physical properties, but manganese may correct the action of sulphur, which is probably present. The alloy resembles nickel in color, it machines well, and takes a high polish and retains it indefinitely. It melts at 1360° C.; has a specific gravity of 8.87 and a hardness number of 20 to 27 on the Shore scale. It is magnetic and absorbs carbon, which can exist in it both free and combined. Compared with nickel and copper its mechanical properties are:

	Copper, rolled.	Nickel, rolled.	Monel metal.		
			Cast.	Rolled.	Annealed.
Tensile strength, pounds per square inch Elastic limit,	34,000	75,500	85,000	100,000	110,000
pounds per square inch Elongation, per	18,000	21.000	40,000	50,000	80,000
cent. in 2 inches Contraction, per	52	43.9	25	30	25
cent	57	57	25	50	50
ticity			22,000,000 to 23,000,000		

Monel metal resists corrosion by sea-water, superheated steam, and chemical solutions about as well as Parson's manganese bronze, phosphor bronze, and Tobin bronze. There is no difficulty in forging and rolling it, but on account of its high melting-point and power of dissolving gases special precautions are needed in making sand castings, somewhat similar to those necessary for making steel castings. These uses are suggested: pump cylinders for seawater, propellers, rudders, mining screens, valves, and plumbing fixtures subject to corrosive influences. Sheets of monel metal are largely used in America for roofing purposes.

Nomenclature of Micro-constituents and the Micro-structures of Steel and Cast Iron. H. M. Howe and A. SAUVEUR. (Rev. de Métallurgie, ix, 983.)-Division into metarals and aggregates is adhered to, and only generally-accepted principles and theories have been considered. First, there is the liquid iron, which forms austenite, cementite, and graphite during solidification. During the transformation of austenite, martensite, troostite, and sorbite are formed as intermediate products; the final products being ferrite and pearlite. Other and rarer constituents are: lederburite (Wüst)—the austenite cementite eutetic; ferronite (Benedicks) —iron containing about 0.27 per cent. of carbon; steadite (Sauveur) —the iron-iron phosphide eutectic; and the three transition products, harenite (Arnold), osmondite (Hev.), and troosto-sorbite (Kourbotoff). The latter is falling into disuse, while osmondite is described as the limiting phase between troostite and sorbite. Manganese sulphide is also included as a nicro-constituent of steel.

Electron Theory of Thermo-Electricity. O. W. RICHARDSON. (Phil. Mag., xxiv, 737.)—The difference between Bohr's results and the author's may arise from neglecting to include effects due to a possible difference in the rate of transference of kinetic energy by an electric current in different materials. In this paper the former calculations are stended to include these effects. It seems probable that effects due to chemical action ought to be included, and recent experiments by Pring and Parker on carbon, and by Fredenhagen on sodium and potassium, strengthen this probability. Richardson thinks that electronic emission may be conditioned by chemical action, but considers that there is considerable evidence in favor of the view that there is an emission of electrons from her conductors which is independent of chemical action.

Electric Furnace for Experiments in Vacuo at Temperatures up to 1500° C. R. E. Slade. (Roy. Soc. Proc., Ser. A. lxxxvii, 519.)—This furnace consists of a platinum tube 2 cm. in diameter and 17 cm. long, with walls 1 mm. thick. This was mounted in water-cooled brass terminals at the ends. By means of a current of 350 to 500 ampères at ¾ volt passed through the tube, the interior of the latter attained a temperature of 1400° to 1500° C. The tube is fitted in an asbestos box filled with magnesia, and the whole furnace is placed under an iron dome. Arrangements are made for evacuating the furnace, for reading the internal pressure, for measuring the temperature by means of a thermo-element, etc. Diagrams are given.



## JOURNAL

OF

# THE FRANKLIN INSTITUTE

DEVOTED TO SCIENCE AND THE MECHANIC ARTS

Vol. CLXXVI

SEPTEMBER, 1913

No. 3

# DESIGN OF LARGE ERIDGES WITH SPECIAL REFERENCE TO THE QUEBEC BRIDGE.\*

BY

#### RALPH MODJESKI, D.Eng.,

Consulting Engineer, Member of the Institute.

It is rather a difficult matter to draw a line between a large bridge and one of ordinary size. My definition of a large bridge would be a bridge which involves a considerable expenditure of money, or presents unusual difficulties of construction, or both. Bridges which by force of circumstances and local conditions span long distances may, therefore, be classed as large bridges. It has been my good fortune to be connected with the design and construction of several large bridges, and I shall deal, in the course of this paper, with the salient features of those structures, while at the same time trying to deduce a few general principles which should govern the design of large bridges. I shall also refer to structures designed by other engineers. It would, of course, be impossible in a single paper to cover the field in detail and in an exhaustive manner; I can only bring out some of the more important questions which should be considered by the designer of such structures. In what follows,

Copyright, 1913, by THE FRANKLIN INSTITUTE.

<sup>\*</sup> Presented at the meeting of the Mechanical and Engineering Section held Thursday, May 1, 1913.

<sup>[</sup>Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.]

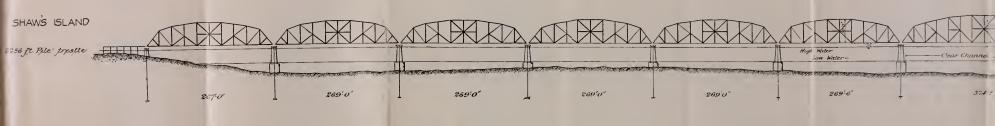
the Quebec Bridge, with its single span of 1800 feet, 100 feet longer than the Firth of Forth Bridge, will be referred to frequently. As that bridge is now under construction, and as the first attempt to build it resulted in a great disaster, the structure will be of particular interest.

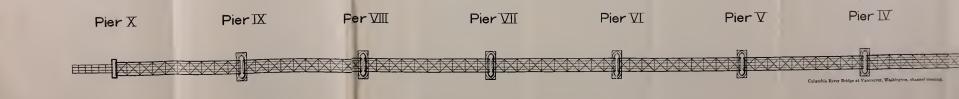
Location.—The first question which the engineer has to deal with, when considering a bridge project, is the location. In the majority of cases this location has previously been fixed, either exactly or within a small range. Whenever this location is not fixed exactly, the engineer makes surveys of the various possible locations, from which surveys preliminary sketches are drawn and estimates prepared. One of the most important conditions to consider in this comparative study is the character of the foundations. Complete borings to determine the kind and quality of the material through which the foundations are to be built, and on which the finished work is to rest, are indispensable. In the case of a railroad bridge it is not always the location giving the cheapest bridge which gives the most economical results. As an instance, let us consider the Celilo Bridge across the Columbia River. A bridge at the Dalles, 12 miles below Celilo, would have been cheaper, but the bulk of the traffic over this bridge being east-bound, the location at Celilo was, on the whole, more economical, as saving about 24 miles in the distance to be traversed by such east-bound traffic. Another important feature in deciding on a location is the permanency of the river bed. A bridge should not be located where there is a reasonable possibility that the stream may change its course. If such a location is unavoidable, the shores should be protected and the river regulated for some distance above the bridge.

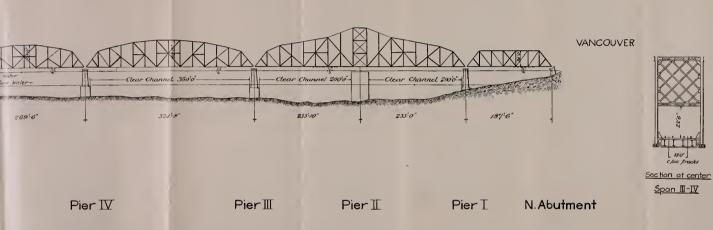
When the location has finally been fixed, more borings should be taken, several at each pier, to establish beyond any reasonable doubt the character of the materials. I am laying great stress on this point, because it is so frequently neglected. Such neglect often results in serious disappointment as to the ultimate cost of the bridge, in differences as to settlement with the contractors, and in delays.

Length of Spans.—While sometimes the length of spans is

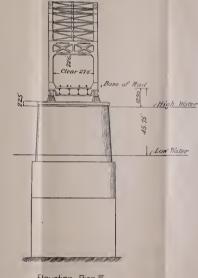
<sup>&</sup>lt;sup>1</sup> The span of the Forth Bridge is sometimes erroneously given as 1710 feet. This is the distance between centres of main end uprights, but the distance between centres of bearings at the bottom chord is 1700 feet.







Columbia River Bridge at Vancouver, Washington, channel crossing.



Elevation Pier III

governed by the cost of the foundations and piers, more often such length of spans is fixed by requirements of navigation or other circumstances. The Government, in giving permission to build a bridge over navigable waters, generally imposes the clear opening of one or more spans, and passes on the design as a whole. It also imposes the minimum clear height above water. Sometimes the ruling of the Government results in an injustice to the railway corporations, as for instance in the case of the Memphis Bridge. The minimum clear height imposed for this bridge by the War Department was 75 feet above highest water known. A clear headroom of 65 feet would have been sufficient, and, if permitted, would only have involved the removal of useless ornaments on pilot-houses of three or four boats, and a provision for lowering the smokestacks on a few boats, similar to the provision existing in the Ohio River, where the required clear headroom above high water is only 53 feet. The additional ten feet not only increased the cost of the bridge considerably, but resulted in heavy grades in the approach in Memphis and a disturbance in street grades.2

Often draw spans or movable bridges are required over streams where there is no navigation, on the theory that some boat might wish to come through some day. But it must be said that in the majority of cases the rulings of the Government engineers are just and necessary for the proper protection of navigation. Where no limitation is placed by the Government as to length of all spans, as in the Columbia River Bridge at Vancouver, for instance, in which only the lengths of the draw span and of the adjacent or raft span were stipulated, the spans should be made of economical length, provided the piers do not reduce the cross-section of the river sufficiently to cause an undesirable increase in the current velocity. This economical length may be determined by trials, and will be attained approximately when the cost of the superstructure and of the substructure are nearly equal. This well-known principle has been applied in determining the length of the six 265-foot spans of the Columbia River Bridge (Plate I).

The charter for the Thebes Bridge provides that it "shall have at least one channel span, with a clear channel way at low

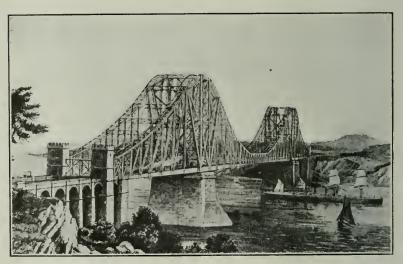
<sup>&</sup>lt;sup>2</sup> See Geo. S. Morison: A Report to Geo. H. Nettleton on the Memphis Bridge, 1894.

Vol. CLXXVI, No. 1053-18

water of not less than 650 feet, and all other spans over the waterway, at a bank-full stage, shall each have a clear channel way at low water of not less than 500 feet, and all such spans shall have a clear headroom of not less than 65 feet, etc." So here the length of spans as well as the clear headroom is definitely fixed by the Government requirements.

In the case of the Quebec Bridge, while the navigation interests fixed the clear height of the structure above high water at 150 feet, the length of span is entirely due to the physical





Original project for the Quebec Bridge in 1884-1885 by Messrs James Brownlee, A. Luders Light, and T. Claxton Fidler.

conditions of the crossing. The stream at this point is narrow and deep, the depth in the centre of the stream being about 190 feet. The current velocity at ebb-tide is very high—about nine miles per hour. Very heavy ice runs at times and tends to gorge. The bed rock, as shown by the borings, while accessible near the shore lines, dips rapidly towards the centre of the stream. All these conditions made it imperative to build a span of great length. The information as to bed rock which we now have would indicate that the original project could have been designed with a somewhat shorter span. Yet we should remember that this original project was undertaken by a private cor-

poration, and we should perhaps recognize the value to it of such advertisement as the building of the longest span in the world would obviously afford. The next longest span is that of the Firth of Forth Bridge, and is 1700 feet long. It is doubtful if a shorter span than 1700 feet would have been practicable at the location adopted for the Quebec Bridge. I consider it perfectly legitimate to build a more expensive structure than economy of the work itself would call for, if the more expensive structure will afford sufficient advertisement and publicity to compensate for the additional expenditure. Cases also often arise where a purely economical and utilitarian structure would be entirely out of harmony with the surroundings. We have a good illustration of this policy in the magnificent stations which the railway companies are constantly building.

A project to build a large bridge at Quebec, presumably in the same location as the present one, was seriously considered in 1884 and 1885. Messrs. James Brownlee, A. Luders Light, and T. Claxton Fidler designed a structure with a clear span of 1442 feet <sup>3</sup> (Fig. 1). The description of that project mentions rock foundations. The more complete information we now have, and which was obtained by a costly series of borings, shows that at the present location rock could not have been attained in both piers with any known method of foundation if the piers had been spaced only 1442 feet apart, even if the great depth of water could have been overcome.

It may be remembered that after the disaster of August 29, 1907, the Dominion Government took up the reconstruction of this bridge. A board of three engineers, including myself, was appointed to design and construct the bridge. After some study of the situation, the board decided that the new bridge should be made wider between trusses and designed to carry heavier loads than those originally contemplated; that, further, none of the old steel work could be used to advantage. It also decided to keep the same location. To discuss the reasons for these conclusions would take up too much space in this paper. The final outcome is a double-track span of 1800 feet, with a width of 88 feet between centres of trusses, designed to carry on each track a live load consisting of two E 60 engines 4 placed in any posi-

<sup>&</sup>lt;sup>5</sup> London Engineering, vol. xxxix, 1885, p. 336,

<sup>&</sup>lt;sup>4</sup> Theodore Cooper's specifications.

tion in a train weighing 5000 pounds per foot so as to produce greatest strains. The old piers were not large enough for the new design and could not, therefore, be used. The centre line of the bridge running north and south the two main piers on each side of the stream will be designated as north pier and south pier respectively. At first the board contemplated building an entirely new pier 57 feet south of the present north pier, and enlarging the foundation of the south pier by sinking additional caissons adjacent to the old caisson. The necessary span length would then have been 1758 feet, and it was on that length of span that tenders were asked. It developed later, from the experience of sinking the north caisson,

FIG. 2.



Aqueduct of Gard at Nimes, France.

that the method proposed for enlarging the south foundation would not be safe, even if it were practicable, and so an entirely new foundation and pier were decided on for the south shore. The new north pier could not be placed farther out in the river because of the sloping bed rock and great depth of water. The south pier could not be placed on the north, or river, side of the old south pier, because of the old wreckage, so it was placed 64 feet 8 inches south of the old pier, or as close as possible to it. Both new piers being placed 64 feet 8 inches south of the old piers, measured between centres, the new span remains 1800 feet long.

The piers are all of granite backed with concrete. There is an increasing tendency now to build everything of concrete. Certainly, concrete is a most convenient material and quite economical. When it comes, however, to providing supports for a very important and expensive structure, cut stone masonry should be used in preference to concrete, except for backing. There are many varieties of excellent building stone on this continent. I have used granite, some varieties of oolitic limestone, also sandstone, which all show excellent lasting qualities in works constructed many years ago, while concrete presents some uncertainties and requires expert care to give good results. Concrete may in ages prove to be as lasting as stone masonry, but as yet we do not know. We know that well-constructed stone masonry will last for centuries. A notable example of this is the great Aqueduct of Gard, built by the Romans in the first century B.C. (Fig. 2).

Types of Superstructure.—Having fixed the span lengths of a bridge, the next thing to determine is the type of superstructure to be used. The various types usually applied to long spans may be classified as follows:

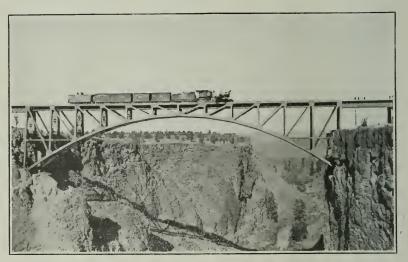
- I. Arches (steel).
  - a. Three-hinged.
  - b. Two-hinged.
- II. Simple spans.
- III. Cantilever structures.
  - a. With suspended span.
  - b. Without suspended span.
- IV. Suspension bridges.

I have purposely omitted masonry and concrete arches as structures not coming clearly within the scope of this paper. Steel arches have a rational application only where Nature has provided natural abutments, as at Niagara Falls, for instance, or where natural surroundings lend themselves to ornamental construction.

Crooked River Arch.—I have recently completed an arch bridge for the Oregon Trunk Railway in the Crooked River Canyon (Fig. 3). It is a two-hinged spandrel braced arch. Three-hinged arches are now seldom used for railway bridges, because they are less rigid than two-hinged arches. They still have a good application in roof trusses which are not subject to heavy and rapidly-moving loads. In several large arch spans the central connection offered considerable difficulties. The reason

is that the top chords at the centre of a purely two-hinged arch are calculated to have stresses in them, due to dead load and temperature, when the span is riveted up and ready to receive the rolling load. These stresses had to be introduced by powerful jacks, or other means, before the final joint could be riveted up. To avoid this difficulty, I have proceeded as follows in the Crooked River arch. It was assumed that the dead load and temperature stresses at 60° F. in the top chord at centre are zero. This being the case, the arch acts as a three-hinged structure under

FIG. 3.



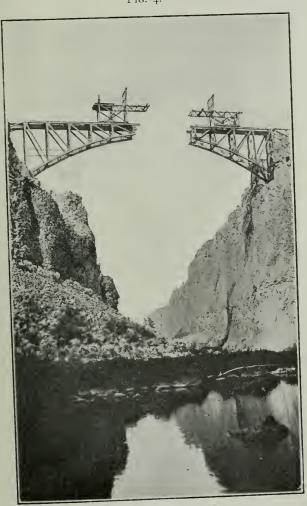
Crooked River arch. View showing completed bridge.

those conditions,—namely, with all dead load in place and at 60° F. The span was therefore erected as a three-hinged arch (Figs. 4 and 5), all dead load, or the equivalent, including the decking, was placed thereon, and at a time when the temperature was very nearly 60° the centre panel of the top chord was inserted and riveted up. The calculations were simple. The dead-load stresses were calculated as in a three-hinged arch, the temperature and live-load stresses as in a two-hinged arch, and the various results combined. This made the erection very simple and the ultimate distribution of stresses more accurate.

A two-hinged spandrel braced arch is probably the best type

to use for railway traffic, where the natural abutments permit of sufficient rise, which will often be the case where the arch type of bridge is a logical solution. This particular type of arch is

FIG. 4.



Crooked River arch under construction.

more rigid and less subject to vibration than the other types of arch, and presents the advantage of easier erection, which can then be simply performed by treating each half as a cantilever arm held back by suitable temporary anchorages until the centre connection is made (Fig. 5).

An arch bridge is a somewhat special structure and rarely used for very long spans, except, as I remarked before, where Nature has provided abutments (Figs. 4 and 6).

Fig. 5.



Crooked River arch. Temporary anchors and adjustments.

Simple Spans.—Twenty-five or thirty years ago the system of truss most favored for long simple spans was a double intersection Pratt truss with parallel chords. Nowadays the type most used is a single intersection Pratt truss with subdivided

Fig. 6.



Berne, Switzerland. A very graceful highway arch bridge.

panels and curved top chord. Fig. 7 shows the former type being replaced by the latter in the Bismarck Bridge (see also Fig. 12). The curved top chord is an element of economy. The single system has also a slight advantage of more definite stresses. It has its disadvantages, such as, for instance, the lack of unifor-

mity in deflection, about which I will speak more in detail in connection with cantilever system. There is no doubt that a bridge composed of simple truss spans is a better bridge than a cantilever system or a suspension design, chiefly because of its rigidity. This rigidity results from the fact that a load placed on one span has no lifting action on the adjacent spans, as in a cantilever system, or on other portions of the same span, as in a suspension bridge. But long simple spans must be erected on falsework or floated into

FIG. 7.



Bismarck Bridge. Replacing old spans by spans of present type.

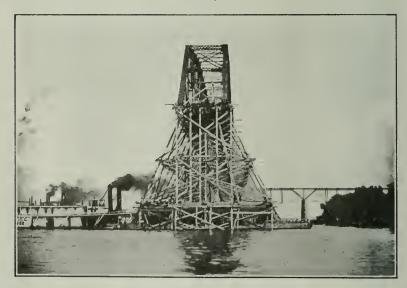
position. The first method is often inadmissible on account of the necessity of keeping the channel open for navigation, as in the Memphis and Thebes Bridges, or excessive depth of water combined with navigation requirements, as in the Quebec Bridge, or other local conditions. The floating of a span into position is not only costly but hazardous. It has been successfully performed, but is not always feasible or safe (Figs. 8 and 9). Then, too, generally speaking, a cantilever bridge is more economical for long spans. These considerations often lead to the adoption of a cantilever design in preference to simple spans. A cantilever span

## Fig. 8.



Floating span into position at Louisville, Ky.

Fig. 9.



Floating span into position at Louisville, Ky.

can always be erected without falsework, although the adjacent or anchor spans must generally be erected on falsework. Sometimes simple spans are erected without falsework. Fig. 10 shows the 340-foot simple span over the main channel and Fig. 11 the 230-foot span of the Columbia River at Celilo, Ore., being erected as a cantilever.

The length of simple spans has been growing from year to year. It may be remembered that the Cincinnati Southern Bridge at Cincinnati, built in 1877, contains a simple span of 515





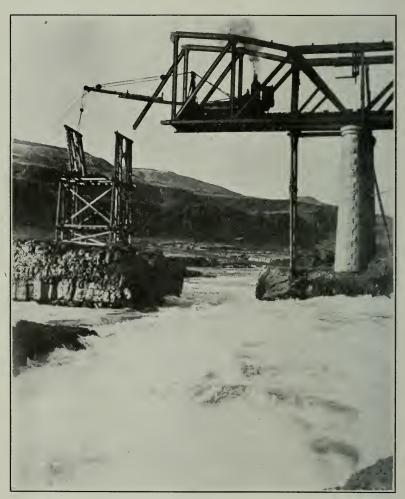
Columbia River Bridge at Celilo, Ore. Main span 340 feet long, being erected by cantilever method.

feet. In 1891 George S. Morison built the Cairo Bridge, containing a span 518 feet in length, single track. The Municipal Bridge in St. Louis has three simple spans of 668 feet in length, 110 feet high at centre, double track and roadways. The Metropolis Bridge over the Ohio River, if the present design is carried out, will have a simple span 720 feet long, double track. This increase is due largely to the use of higher grade materials, such as nickel or chrome-nickel steel, and to the improvement in shop and field methods.

And here we may say a few words about wind forces. In

small spans the action of wind rarely affects the main members of the span, and the wind-bracing used is calculated more to make the structure rigid against lateral motion under rapidly-

Fig. 11.



Columbia River Bridge at Celilo, Ore. One of the 230-foot spans being erected by cantilever method.

moving loads than to take care of actual wind stresses. As the length of span increases, this element of wind becomes more and more important, until in very long spans it may become as

important as the moving load. In a simple span the heaviest members, as well as the greatest height of truss, occur near the centre of the span. In other words, the resistance to wind per lineal foot of truss in a simple span is greatest at the centre of the span, and, owing to the overturning moment due to wind, grows in importance with the height. In a cantilever span the greatest height of truss and the heaviest members are near the piers, hence the greatest resistance to wind per lineal foot of truss is near the piers. This remark is sufficient to explain

FIG. 12.



McKinley Bridge across the Mississippi River at St. Louis. One of three 518-foot spans.

why wind stresses are easier to provide for in a cantilever structure than they are in a simple span of the same length.

I shall return later to wind forces and their importance while discussing provisions made for wind in the Forth and Quebec Bridges.

Longest Simple Span.—No hard-and-fast rule can be laid down as to the length at which a simple span becomes uneconomical as compared with a cantilever span. Generally speaking, considering the present knowledge of materials, a simple span of 700 feet may be taken as the practical economical limit, beyond which it is not advisable to go without a thorough investigation and comparison with a cantilever system. Where con-

ditions require unusual methods of erection this limit may be much lower. For instance, in the Thebes Bridge (Plate II) it was necessary to erect the 671-foot channel span without falsework (Figs. 13 and 14). A simple span would have required the addition of a considerable amount of metal, both in the span itself and in the adjacent spans, to permit of its being erected as a cantilever; this excess of metal would have been useless after the completion of the bridge, and its cost would have made the

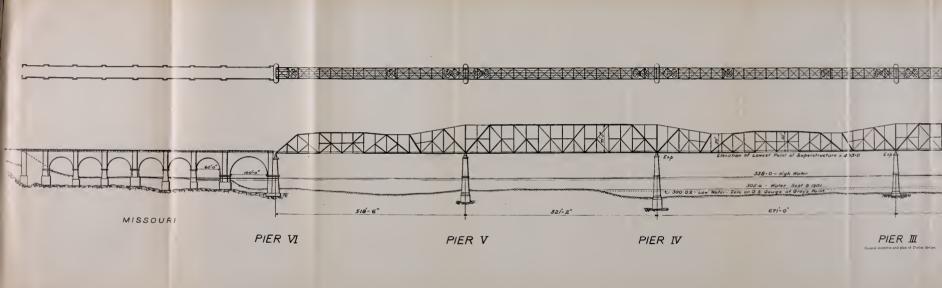
Fig. 13.



Thebes Bridge. Erecting main span by cantilever method without falsework.

bridge more expensive than the adopted cantilever design. This was shown to be true by careful estimates made at the time.

General Dimensions of Simple Spans.—In designing long simple spans the following general principles should be observed. The width, centre to centre, of trusses should not be less than one-twentieth of the span, preferably one-eighteenth. In double-track spans the width required for clearance generally governs, except in very long spans. The height at centre of span, for a Pratt system of truss with subdivided panels, should be from one-seventh to one-fifth of the length. The table below shows the proportions of the width and height to the length of span in some of the curved top chord bridges built recently:



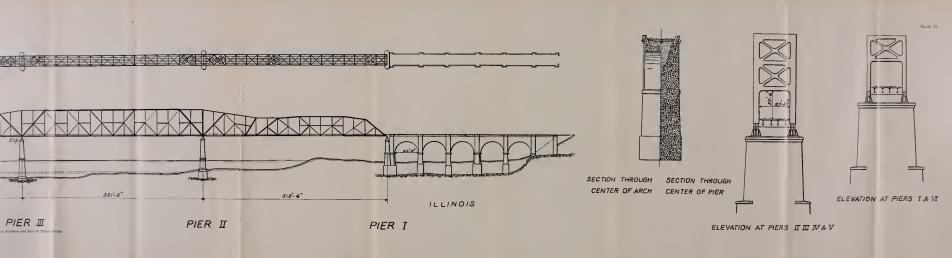


TABLE I.

PROPORTIONS OF SIMPLE SPANS WITH CURVED TOP CHORDS.

	Per cent. ratio height to length	Per cent. ratio width to length
Municipal Bridge, St. Louis, Mo	16.47	5.24
Cincinnati, Ohio, over Ohio River	15.41	5.60
Pennsylvania Railroad, over Delaware, Philadelphia	15.76	5.82
Ohio Connecting RyPittsburgh	14.53	5.57
McKinley Bridge, St. Louis, Mo	15.07	5.73
Merchants Bridge, St. Louis, Mo	14.47	5.8o
Mobridge, Mo	15.18	5.48
New Bismarck Bridge, N. D	16.25	5.50
Quebec suspended span	17.19	
Thebes suspended span	15.03	
Average	15.56	

The height at the ends should be only sufficient for an effective portal. A rigid mathematical research by Mr. Joseph Mayer, principal assistant engineer of the Quebec Bridge, leads to a theoretical proportion between the height at centre and length of span equal to .18, or somewhere between one-fifth and one-sixth, for heaviest loads and double-track spans.

Panel Length.—The best panel length is not so easy to determine. Since the economical inclination of diagonals is very nearly 45°, it would result that in a Pratt truss with subdivided panels their length should approach one-half of the height of truss. This would mean that in a truss with a curved top chord the panels in the centre should be longer than those near the end. This has been done at least in one instance, namely, in the Municipal Bridge in St. Louis. The advantages of such an arrangement are a slight economy in the weight of steel and an improved appearance, since the diagonals have nearly the same inclination throughout. The equal panels, however, present, in my opinion, two decided advantages, which may more than offset the advantages of the former system, namely, that, all panels being equal, there is a greater duplication of parts, the floor beams are all alike, except at ends, the stringers are all alike, the length of bottom chord eyebars is the same throughout; and, further, that the falsework may be built in uniform panels, and the traveller, which is usually designed with a view

to have the uprights in proper relation to the panel points, so that the connections may easily be made, preserves its relation to the various panel points as it is moved from panel to panel.

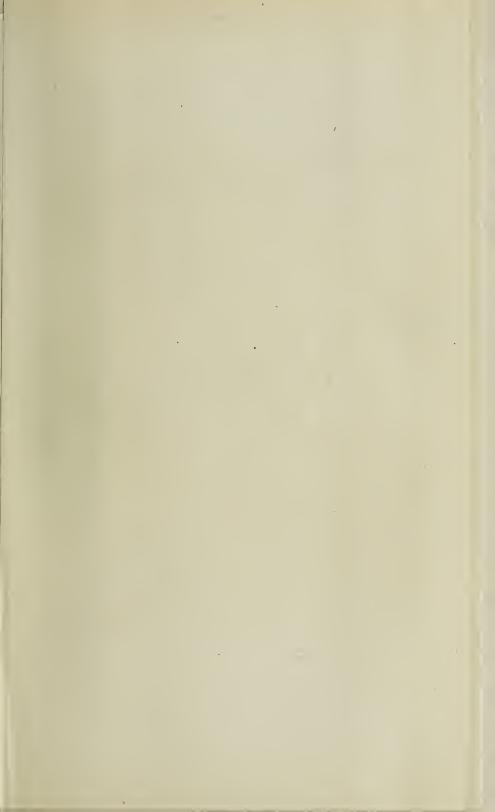
Fig. 14.

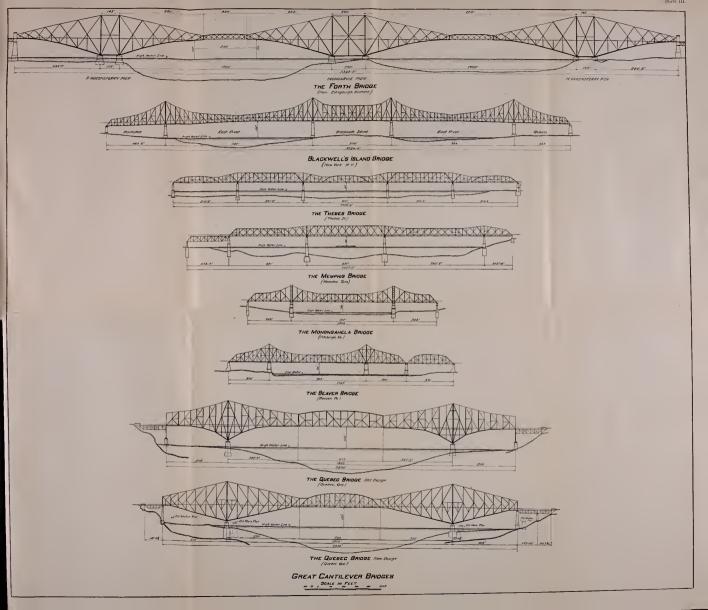


Thebes Bridge. One of the eight adjustment wedges by means of which the projecting arms were lowered and central connection made.

For these reasons, uniform panels should be preferred in the majority of cases of simple spans.

I have already stated that the greatest practical length of a





simple span is about 700 feet. With the use of certain known alloys of steel of greater strength than medium carbon steel this limit may become as much as 750 feet. Beyond this limit the weight of simple spans becomes so great, in comparison with cantilever spans, that the latter must be considered. A mistaken idea sometimes prevails that the weight of steel in a span increases in proportion to the square of the length. This is, in a measure, true for short spans, say 100 to 300 feet. This ratio of increase, however, is not a constant, but increases with the span. simple span above 1200 feet in length increases in weight approximately as the cube of the length, and this exponent increases more and more rapidly until at about 2000 feet the weight of carbon steel required to carry the weight of such a span and of a moderate live load becomes infinite. For a span built of nickel-steel the weight becomes infinite when the length reaches 2700 feet. Simple spans much below those limits, even if possible, would still be very uneconomical until we get down to spans 700 feet or under.

Cantilever Spans.—This leads us to cantilever spans (Plates III and IV). I mentioned two types of such spans: one without a suspended span, and the other with a suspended span. A remarkable example of a cantilever bridge without a suspended span, which may be called a semi-continuous structure, is the Blackwell's Island, also called the Oueensboro Bridge, in New York. There seems to be no advantage in omitting the suspended span; on the contrary, the structure differs from a true continuous bridge over several supports only by the introduction of a hinge at the centre of the main span which transmits shears but not moments. The vibrations and deflections of each segment are, therefore, transmitted through those hinges to all the other segments. Furthermore, since the stresses in such a structure depend on deflections, there is more or less uncertainty in the calculations. I do not wish to be understood as objecting to any type of structure seriously, because of the uncertainty of calculations. In any logical construction the calculations can always be made with sufficient accuracy for the safety of the work. It is only when everything else is equal that determinate stresses should be preferred.

Let us consider the usual type of cantilever bridges, the one in which two cantilever arms support a suspended span. We

Vol. CLXXVI, No. 1053—19

may assume that in bridges requiring the construction of a cantilever span the length of the main span is usually determined by local conditions. The general dimensions to be fixed by the designer are, therefore, the length of the suspended span, the length of the anchorage spans, when these are not determined by local conditions, the height of the trusses at various points, the relative distances and positions of trusses to each other. Let us discuss these various dimensions in connection with the new Quebec design (Fig. 15). The Quebec Bridge, with its longest span in the world, has justly attracted much attention among engineers and has naturally elicited comment and criticism. It is acknowledged that a discussion of a scientific subject by professional men is often of greater value than an elaborate paper on this same subject by one individual. If I refer to some of the criticisms, let it be considered as a friendly discussion which may be of value to the profession.

General Description of the New Quebec Bridge.—The new Quebec Bridge has been finally designed with two anchor arms 515 feet long, a suspended span 640 feet long, and two cantilever arms 580 feet long. The moving loads finally adopted for the Quebec Bridge are: on each track two Cooper's Class E-60 engines, followed or preceded, or followed and preceded, by a train load of 5000 pounds per foot per track. In addition to the actual dead load of the structure, a load of 500 pounds per lineal foot on suspended span and 800 pounds on balance of bridge was allowed for snow.

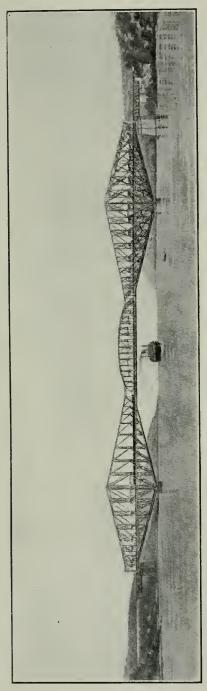
Wind Loads.—The wind loads were taken as follows: A wind load normal to the bridge of 30 pounds per square foot of the exposed surface of two trusses and one and a half times the elevation of the floor (fixed load), and also 30 pounds per square foot on travellers and falsework, etc., during erection.

A wind load on the exposed surface of the train of 300 pounds per lineal foot applied nine feet above base of rail (moving load).

A wind load parallel with the bridge of 30 pounds per square foot acting on one-half the area assumed for normal wind pressure.

In the Forth Bridge the enormous wind load of 56 pounds per square foot was assumed. This load was imposed on the designers by the Board of Trade soon after the Tay Bridge





Quebec Bridge. Length of main span, 1800 feet. Clear height above high water, 150 feet.

disaster. The Tay Bridge was not designed to withstand even a 30-pound pressure. This assumption of a 56-pound wind in the Forth Bridge results in a very large addition of metal in the bottom chords through which the wind stresses are transmitted to the piers. The material in those members is distributed as follows:

Dead load	2282 gross tons
Live load	1022 gross tons
Wind load	2920 gross tons
Total	6224 gross tons

The metal here provided for the wind is nearly three times that provided for the live load, and is about 47 per cent. of the total required.

In the New Quebec Bridge design the wind pressure is equivalent to about 35 per cent. of the uniform live load near the piers and to about 20 per cent. of the live load near the ends of the cantilever arms.

A pressure of 30 pounds, according to German experiments with electric cars, would correspond to a wind of a velocity of over 100 miles per hour. Other experiments made at various times on small surfaces show that a velocity of 85 miles would correspond to a pressure of about 30 pounds.<sup>5</sup>

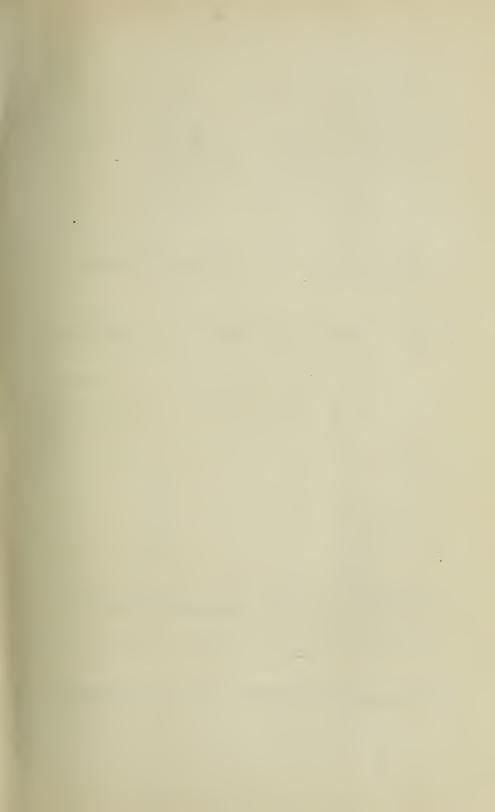
The following formula for wind pressures is generally used:

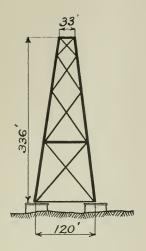
 $P = kv^2$ 

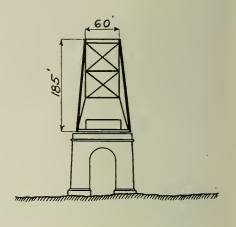
in which P = pressure per square foot,  $\tau' = \text{velocity in miles}$  per hour, and k = a coefficient.

Eiffel's two hundred or more experiments show this coefficient to vary from 0.0026 to 0.0032, and the average is 0.0030, which he recommends. Trautwine makes k = 0.0050, which seems too high. But, even using the latter, a pressure of 32 pounds would correspond to a "hurricane" of a velocity of 80 miles. The German experiments agree with Eiffel's. Making k = 0.0030, a pressure of 30 pounds would correspond to a velocity of 100 miles per hour, which, according to Trautwine, is a violent hurricane uprooting "large trees."

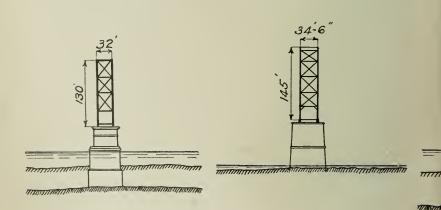
<sup>&</sup>lt;sup>6</sup> See Captain Bixby's able research on wind pressure experiments in Report of Engineer Officers as to Maximum Span Practicable for Suspension Bridges.



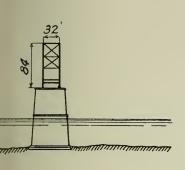


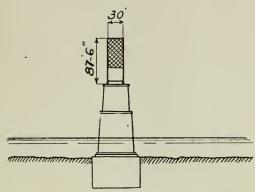


FORTH BRIDGE BLACKWELL'S ISLAND BRIDGE



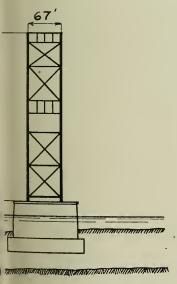
MONONGAHELA BRIDGE BEAVER BRIDGE

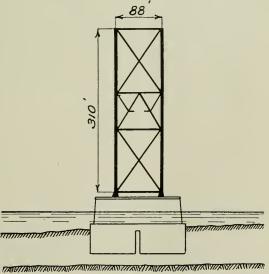




HEBES BRIDGE

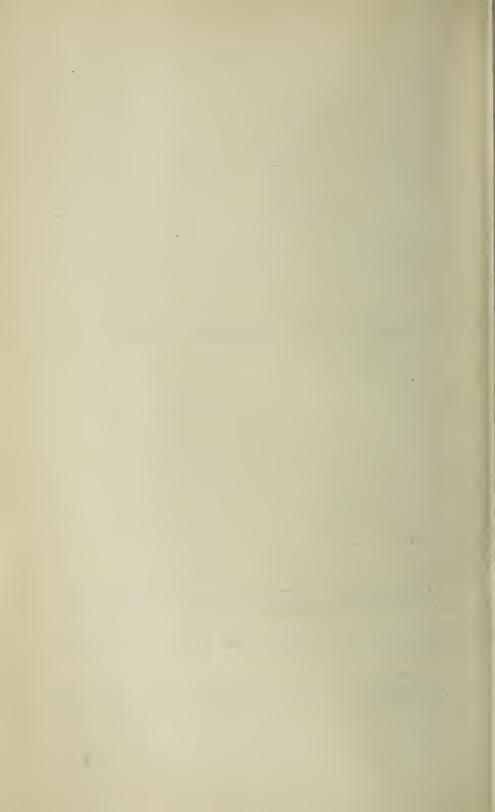
MEMPHIS BRIDGE





DID Design

QUEBEC BRIDGE (New Design)



With a wind of this velocity there would be no traffic on the bridge—empty freight cars or even light passenger cars would be overturned. Velocities of over 85 miles may occur in cyclones and tornadoes over restricted areas. Such storms are very rare in Canada; but even should such an extraordinary disturbance happen, causing a wind pressure of as much as 60 pounds to be applied to the entire Quebec Bridge as now designed—the stresses in the truss members would be less than with the maximum live load and a 30-pound wind—and although the stresses in the laterals would be increased above the specification limits, they would still remain within the elastic limit of the members.

Length of Suspended Span.—The length of the suspended span does not depend merely upon the most economical distribution of material required for carrying the live loads and the dead load of the bridge after it is completed. Where there are no other considerations beyond the actual working stresses in the finished structure, the most economical length of the suspended span for a total span of 1800 feet would be in the neighborhood of 1000 feet. But to erect a simple span of such unprecedented length, either by floating or by cantilever method, would be impractical. Furthermore, the cantilever method of erecting a suspended span of even a moderate length always requires additional material, both in the cantilever arms and in the suspended span, to take care of the erection stresses. The longer the suspended span in relation to the total main span, the greater will be the required addition—so that whether it be contemplated to erect the suspended span by cantilever method or by floating into position, the length of the suspended span finds itself limited not by mere economic considerations of the finished bridge, but by either the excess of material required during erection by cantilever method, and difficulties arising therefrom, or by the difficulties attending the floating of a very long and heavy span into position. These difficulties increase very rapidly with the length of the span to be floated. In the new design the suspended span is the longest which the board considered safe to float, and it fits the entire design very well. The erection of this span by floating made it possible to design it with the view to greatest economy. Its various members will not be subjected to any greater stresses during erection than they would be in a simple span of the same length resting on two piers. It was,

therefore, possible to design it as economically as to weight as a well-designed simple span would be. It is more important to save weight in a suspended span than in an independent simple span, because each pound in the former requires several pounds in the entire structure to carry it. The importance of economy in the suspended span of the Quebec Bridge will be appreciated when it is considered that one pound uniformly distributed over the trusses of the suspended span needs 3 pounds of metal added to the bridge to carry it, making an addition of 4 pounds in all. This accounts for curved top chords in the span in question, as well as for the use of nickel-steel for the trusses thereof.

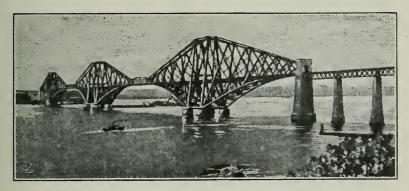
Length of Anchor Arms.—It has been pointed out that the length of the anchor arms is uneconomical—that a shorter arm would have been cheaper. It must not be forgotten that a shorter anchor arm increases the pier reactions, as well as the steel in the anchorage proper. The present anchor piers are founded on rock ledges which dip rapidly toward the river. To move them nearer to the river would have involved much more expensive foundations.

It may be remarked here that, while an addition of dead load in the main span will require several times the weight of metal to carry it, an addition of dead load in the anchor arm requires no increase of metal to carry it when there is an upward or negative reaction on the anchor pier. This is explained by the fact that any load placed between the main piers or on the main spans increases all moments and shears over all the spans, while any load placed on the anchor arm, if the reaction on the anchor pier is negative, decreases that reaction and consequently the moments in the anchor arm, but has no effect whatever on the main span. For this reason carbon steel will be used mostly in the anchor arms of the new design. The carbon steel unit stresses adopted for the Ouebec Bridge are generally fivesevenths of the nickel-steel stresses, the former requiring heavier members. This additional weight in the anchor arms is a source of economy when the relative prices of carbon and nickel-steel are considered.

Height Over Piers.—An opinion has been expressed that the height over the piers of the new Quebec Bridge is not great enough for economy. Actual calculations show that for economy the height of 310 feet in the Quebec design is too great by about

20 feet for the "K" system of trussing adopted; further, that this height would have been at least 40 feet too great for the original system of the official design. The height of the Forth Bridge towers, while 26 feet higher than the Quebec Bridge, though the span is 100 feet shorter, is no doubt economical for the form of trussing adopted for it. The economical height is not only a function of the length of the span but also of the panel length next to the pier. This height should be such as to correspond to an inclination of the diagonals not far from 45°. A double intersection system with very long panels near the pier, such as adopted in the Forth Bridge (Fig. 16), would have been economical for the Quebec Bridge, except that it

FIG. 16.



Forth Bridge.

requires a system of secondary members or sub-posts, or very heavy longitudinal girders, or both, to carry the load from panel to panel. Then, too, it is well to reduce in the members the stresses due to their own weight—which in long panels become quite important. The 20-foot excess in height of the present Quebec design over what would have been the economical height is justified by the resulting reduction in the sections of the bottom chords, which are of considerable size at best.

Straight versus Curved Chords.—In long cantilever spans the bottom chords of the cantilever and anchor arms should be straight when possible. With a curved chord the joints must be made at the panel points. These joints are of great importance, as has been shown in the Report of the Royal Commission on the Quebec Bridge Disaster. They should be fully spliced

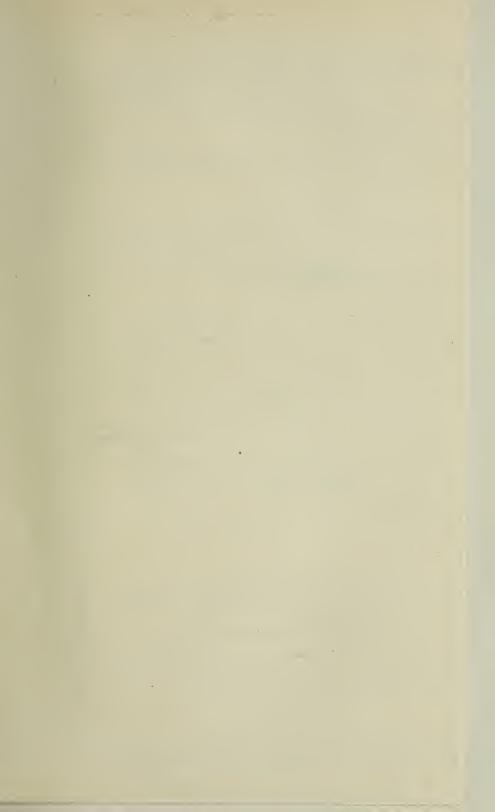
to take care of secondary stresses due to deflections of the span during erection and under the action of live load. It is advisable, therefore, to place them outside of the point of connection with the diagonals and keep them clear of gusset plates. The same objection does not exist in top chords of simple spans, which are of moderate sizes, even in the longest spans known. The economy in simple spans resulting from such curved chords is worth while and quite important, while if any economy were to result from curving the bottom chord of the cantilever and anchor spans, such economy would certainly be of little importance in comparison with the resulting disadvantages. The vertical deflections from live loads are not as great in a straight chord design as in a curved chord design. Another consideration in favor of the straight chords is that the most important, in fact the bulk, of the wind forces travel to the pier through the bottom chords of the cantilever and anchor arms and the wind-bracing, or lateral system situated in their plane. The straight bottom chords carry these stresses direct to the piers without transmitting any appreciable components to the web system of the trusses. Not so with curved bottom chords. At each joint where the chord's direction is changed a component stress is transmitted to the web. This means that while a pair of straight chords with its lateral system deflects under the action of the wind in the plane of the chords only, a pair of curved chords, by transmitting shear to the web members, causes the trusses to deflect, the windward truss downward, tending to flatten the curve, and the leeward truss upward, tending to make the curve more pronounced. The rigidity of the straight chord design against lateral deflections and oscillations is therefore greater than that of the curved chord design.

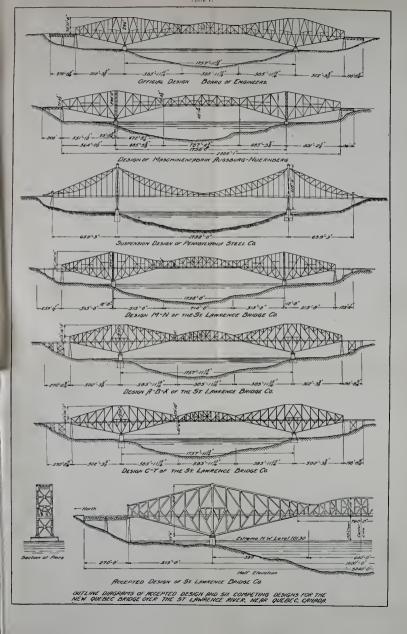
One of the reasons why curved bottom chords were used in the cantilever arms of the original Quebec Bridge design was the fact that it was the aim of that design to provide full headroom of 150 feet on a width of 1000 feet. The bottom chords of the anchor arms were then made curved also for the sake of symmetry. This width on which the full headroom will be obtained has been reduced in the new design to about 760 feet, which certainly is more than ample to accommodate navigation. Only the highest vessels will be limited to this width of 760 feet, and that only at high water.

The top chord of the Quebec Bridge cantilever and anchor arms is straight. The Forth Bridge cantilever arms have straight top chords also. While there was good reason for making the Forth Bridge top chord straight, there was no serious reason, beyond a slight increase in vertical rigidity, for making it straight at Quebec. The two trusses on the Forth Bridge are in planes inclined toward each other at the top. The two top chords are parallel. Had they been made curved they could not have been parallel, since they must necessarily be situated in the inclined planes of the trusses. The appearance of tension chords having a greater distance apart at the centre of the arm than at either end would have been very bad. But there is no such reason at Ouebec. The trusses are in vertical planes and the top chords could have been curved without serious inconvenience. but also without any advantage. The board considered that, aside from the additional vertical stiffness, a straight chord will present an appearance of strength which a curved chord would not do.

Relative Position of Trusses.—With regard to the distance between trusses and their position relative to each other, the trusses of the new Quebec Bridge will be in two vertical and parallel planes. The distance, centre to centre, of trusses will be 88 feet. One of the first preliminary sketches made after the board was created contemplated placing the trusses in planes inclined in the same manner as in the Forth Bridge, namely, with the tower posts converging toward the top and the bottom chords of both the anchor and the cantilever arms converging toward their respective ends. Another sketch contemplated trusses in vertical planes, but converging for the anchor and cantilever arms toward their respective ends. Both these plans would be economical in the amount of metal required in the finished bridge; but erection of a structure of this magnitude is extremely difficult, and some sacrifice of economy is necessary to make the field work as safe and easy as possible. It was during the erection that the old Quebec Bridge collapsed. The board consulted several of the best authorities on erection of large structures, and, while their opinion differed somewhat, it was decided, after much deliberation, to make the trusses parallel throughout. In doing so we had in mind not only the erection which was the principal consideration, but the greater

simplicity of details at such important points as the pier posts and the points of suspension of the suspended span. The connections at these points become quite complicated when the anchor arm, cantilever arm, and suspended span trusses are not all in the same plane. It would have been possible to design the bridge with trusses in two planes inclined toward each other, parallel to the axis of the bridge and passing through the end supports of each truss. In this manner all connections of truss members would have been nearly as simple as in the adopted design. Such a design was also suggested and considered. But it was soon decided that the erection of heavy members in an inclined plane of the truss would be too hazardous, and this plan was abandoned. A question may fairly be asked: Since the Forth Bridge, with its curved bottom chords, inclined and flaring trusses, has been so successfully constructed, why was it not possible to follow a similar design in the Ouebec Bridge? The difference is all in the labor conditions prevailing on the two continents at the respective times of building these bridges. the Forth Bridge 3200 to 4100 men were employed when the work was proceeding full swing; their number attained 4600 for a short period. At Ouebec such a large force could not be mustered. The contractors contemplate now using approximately 400 men in the field and not over 1000 including men in the shops. In the Forth Bridge the material was all manufactured at the bridge site. By using a large force of men it was possible to build up the various members of single plates or shapes so that no heavy pieces were handled. The admirable design, consisting principally of tubes, of which there are nearly six miles in the bridge, was built up in a similar manner as boilers are made—piece by piece. The various connections were laid out in the field, plates bent to suit, drilled and riveted on. This method of procedure would be impossible in Ouebec. Not only are the men not available, but while on the Firth of Forth the climate is such that work may go on at all seasons of the year. in Ouebec work aloft is impossible during more than seven months in the year. Here, then, the bulk of the work must be done by machinery to save manual labor, and must be done in the shops to permit a continuous progress. The work in the field must be reduced to the minimum or to the assembling of large pieces—as large as it is practicable to handle. The Amer-





ican type of pin-connected construction lends itself best to these conditions, but with that type the details will be much simpler and the erection much easier with trusses situated in two vertical and parallel planes.

System of Trussing.—The system of trussing was from the beginning the object of discussion and diversity of opinion among the members of the board; so much so, that before a definite agreement was reached it was decided to work up a plan which, though not satisfactory to all the members of the board, would, when detailed, give the first accurate estimate of weights, which would be also sufficiently accurate to serve as a start in designing any other plan of the same general dimensions. The plan thus detailed, though not approved, will be referred to as the official design. A discussion of the proceedings among the members of the board and the government officials, which led to the ultimate result, would be out of place here. Let it suffice that, in addition to asking for tenders on the official design, the bidders were requested to submit their own designs in accordance with specifications furnished by the board. The time allotted for preparing such designs was shorter than the time it took the board to prepare the official design; but it should be remembered that the official design furnished to the bidders information which it took months of study to prepare. Not the least important information thus furnished was the estimate of weights computed from the details of the official design.

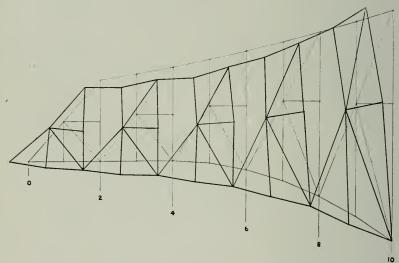
Selection of Design.—Several designs were submitted with the tenders (Plate V); the design submitted by the St. Lawrence Bridge Company, with what may be called a "K" system of trussing in the cantilever arms and anchor arms, was finally recommended by the majority of the board and later endorsed by an enlarged board appointed by the Minister of Railways and Canals for the special purpose of selecting the best tender. The main reasons for recommending the design in question are given in the enlarged board's report as follows:

(a) The type of design offers greater safety to life and property during erection, as well as economy and rapidity in construction.

<sup>&</sup>lt;sup>6</sup> House of Commons Debates (Canada), Tuesday, April 19, 1912, vol. xlvi, No. 65, p. 5522 and following.

- (b) The design contains the minimum number of secondary members and requires few, if any, temporary members during erection.
- (c) The system of triangulation, by dividing the web stresses, reduces the members to more practical sections and simplifies the details of connections.
- (d) The design economizes material, as shown by the calculated weights of the two designs.
- (e) The general appearance of the structure is, in our opinion, improved.

FIG. 17.



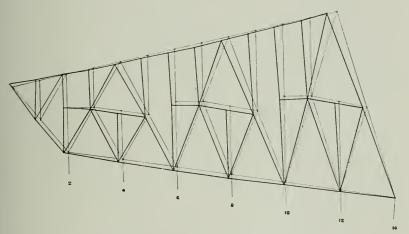
Quebec Bridge, Phœnix Bridge Company design. Deformation diagram. Live load reversed.

Scale of deformation is 120 times greater than scale of truss.

There are two advantages of this "K" design which are not clearly brought out in the above reasons, and on which I wish to lay considerable stress, namely, uniform deflections and regularity of erection operations from panel to panel. The uniform deflections can best be seen by comparing the Williott's diagrams. Figs. 17 to 22 show the deflections of the anchor arm under dead load and under dead and full live load in the old, the official, and the final designs. The deformations are, of course, on an exaggerated scale. A comparison of these diagrams will show that secondary members, or those which receive their

maximum stress from partial live load only, such as the vertical suspenders carrying one panel of floor (Figs. 17 and 18), or members which carry dead load only, such as vertical sub-posts supporting the top chord, or members which normally have no stress in them, such as struts which serve to reduce the unsupported length of main compression members, are the source of local bending in the main members to which they connect. This is because the variation in length of the secondary members as the loads are applied is independent of the variation in length of the main members. For instance, a secondary member car-

Fig. 18.



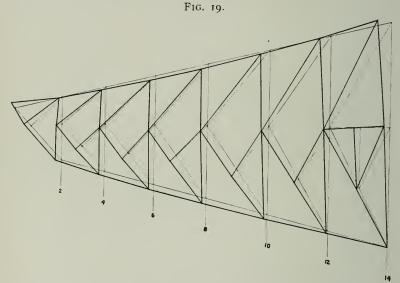
Quebec Bridge, official design. Deformation diagram. Live load reversed.

Scale of deformation is 120 times greater than scale of truss.

rying dead load only receives its full deformation in length when the span is finished, but its length remains constant under any condition of live load, while the adjoining main members compress or elongate with each application of live load. In the same manner a suspender carrying one panel of the floor, for instance, will receive its maximum elongation under concentrated live load in this panel whether the remainder of the bridge is loaded or not, while the adjoining main members will receive their maximum deformation under quite different conditions of loading. The bridges are generally designed in such a manner that the secondary stresses are either entirely eliminated or largely reduced when the main members are subject to

greatest direct stresses. This is done by determining the lengths of the various members, both main and secondary, in such a way that the truss, under the maximum load, will assume as nearly as possible the geometrical shape. This requires, however, an initial displacement of the main members, which during erection may be very objectionable.

The diagrams referred to show the situation as reversed, namely, as if the loads were applied to a truss having the true geometrical form. In order to obtain the true geometrical form,



Quebec Bridge, St. Lawrence Bridge Company design. Deformation diagram. Live load reversed.

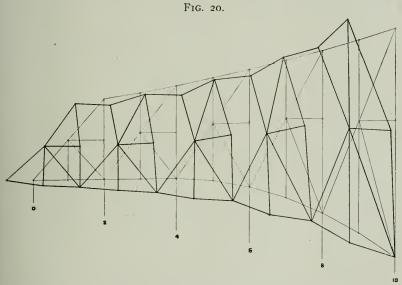
Scale of deformation is 120 times greater than scale of truss.

after the loads are applied, we should begin with a truss deformed under condition of no load.

The comparatively large distortions of the truss in the old design (Figs. 19 and 20) are due not only to greater unit stresses used but also to the curved bottom chord and the large number of secondary members. I have explained the reason why curved bottom chords were used in that design. Of the three designs shown in the diagrams, the new design has the least number of secondary members. It should be remarked that the same advantage could have been obtained with a double intersection

Warren truss by arranging the panel lengths in such a manner as to eliminate the intermediate vertical secondary members supporting the chords. (See Memphis and Forth Bridge diagrams, Plate III.) It would be interesting to know the extent of secondary bending stresses produced in the tubular bottom chords of the Forth Bridge by those vertical members, but unfortunately the necessary data for their calculation are not available.

The regularity of erection operations consists in the fact



Quebec Bridge, Phœnix Bridge Company design. Deformation diagram. Dead + live load reversed.

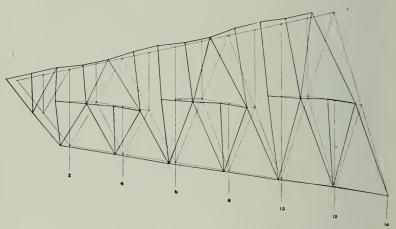
Scale of deformation is 60 times greater than scale of truss.

that, starting from the pier, the position of members in each panel in the "K" design is just like the preceding one, and that coupling up of members in each successive panel, as the traveller moves forward, requires the same succession of motions as in the preceding one, except that pieces become lighter as the erection proceeds. Experience shows that the oftener an erection crew goes through a series of the same motions, as, for instance, in erecting a succession of simple spans all alike, the more rapid their progress becomes.

Some of the more important features of the Quebec design

will be of interest. The lateral wind-bracing has been omitted between the top chords of the cantilever and anchor arms. All wind forces are taken directly to the pier through substantial bracing between the bottom chords. This arrangement not only makes the distribution of wind stresses perfectly definite but permits the spreading of tracks to 32 feet 6 inches, centre to centre, instead of the usual 13 or 14 feet, which results in a saving in the floor system, and consequently in the entire structure. With the tracks spread, a load on one track only produces a torsion in the cantilevers, and the presence of wind-bracing

FIG. 21.



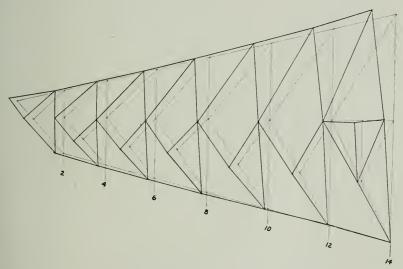
Quebec Bridge, official design. Deformation diagram. Dead + live load reversed. Scale of deformation is 60 times greater than scale of truss.

between the top chords would produce undesirable and excessive stresses which would have to be taken care of by a large addition of metal to the lateral and sway systems and to the trusses.

The floor system is of carbon steel throughout. It is, therefore, stiffer than if made of nickel-steel. The long floor beams deflect less and the secondary stresses produced by their deflection are thus reduced. Even then some of the connections of floor beams to posts had to be made by means of pins. The top chords of the cantilever arm and of the anchor arm as now designed are of carbon steel eyebars. The originally-submitted design contemplated nickel-steel plates riveted throughout for the cantilevers, and carbon steel plates for the anchor arms. By

substituting eyebars a better design is obtained and much easier erection assured, and, although nickel-steel is replaced by carbon steel in the cantilever arm, the substitution results in a saving when both the cantilever and anchor arms are considered. Carbon steel will be used in the entire anchor arm, in the top chord and pier members of the cantilever span in the top lateral system of the suspended span, in all the floor system and all sway bracing. Nickel-steel will be used in the trusses and bottom laterals of the suspended span, in the trusses except top chords and pier members, and in the lateral system of the cantilever





Quebec Bridge, St. Lawrence Bridge Company design. Deformation diagram. Dead + live load reversed.

Scale of deformation is 60 times greater than scale of truss.

arms. The anchor bars which hold down the ends of the anchor arms have been made very long to reduce bending stresses from expansion.

The suspender eyebars which support the suspended span are subject to oscillation in the plane of the trusses, due to expansion. A total expansion of 16 inches must be taken care of at these two points of suspension—besides the extension of the bottom chords under the live load. Manganese bronze bushings will be provided in these eyebars to permit of easy turning on

Vol. CLXXVI, No. 1053-20

the pins. But, even should these fail to turn, there is sufficient metal in these eyebars to prevent overstress from bending.

Friction brakes will be installed to prevent excessive longitudinal oscillations of the suspended span under tractive forces of trains.

All latticing of compression members is designed in proportion to the sectional material of each member. The latticing is made strong enough to transmit in transverse shear 2 per cent. of the direct stress of the member.

Determination of Dead Load.—After the designer has determined the principal dimensions and has designed the skeleton outline of the bridge, the next necessary step is to calculate the stress sheets and proportion the various members. Assumptions must first be made on the dead load of the various portions of the span. In simple spans and in suspension bridges a first assumption of a uniform load per foot is generally sufficient except in very long spans, in which the concentrated loads should be calculated after the details are designed, and the sections should be checked and modified if necessary. In cantilever structures the distribution of the dead load is quite far from uniform (Fig. 23).

The Forth Bridge weighs 2 tons per foot at the centre of each span and 13½ tons per foot near the towers. The new Quebec Bridge weighs 8.7 tons per foot near the centre and 38 tons per foot near the piers. The original Quebec Bridge was underestimated—the calculated dead load stresses were too small; it was to guard against a similar error that the official design of the new bridge was worked out in detail before even the system of trussing was quite agreed upon.

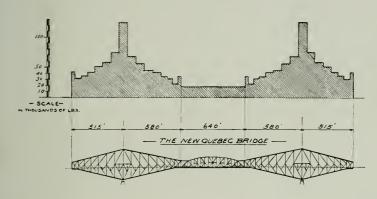
In calculating the weight of a span from the known weight of a shorter span it is customary to assume that the total weight of steel in trusses and bracing increases as the square of the span. This rule of thumb is sufficiently correct for small spans, not to exceed 200 or 300 feet in length, but is obviously wrong for very long spans. If it were true for all spans, then a span 10,000 feet in length could be built by providing 100 times more metal than a span of 1000 feet would require. We know that a span of such length is impossible with materials now known and that it would fail under its own load. As a matter of fact, in a cantilever system of the size of the Ouebec Bridge the

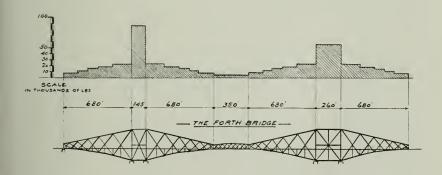
weight of the steel increases more rapidly than the cube of the length. This power or exponent increases still further for longer spans until it becomes infinite for a span which is just long enough to carry its own weight only at the allowable unit stresses without being able to carry any live load.

FIG. 23.

— <u>DIAGRAMS of WEIGHTS</u>—

<u>PER FOOT of BRIDGE</u>





The principal dimensions being fixed and the preliminary stress sheets calculated, the details of the structure must be worked out. Needless to say that all these determinations which I have mentioned as taking place in succession are correlated to each other, and frequent retracing of one's steps is necessary

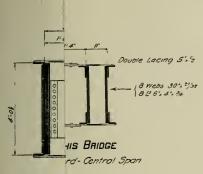
before the detail plans are matured. The general order of procedure, however, is always about as described.

Bottom Chords.—The bottom chords of the anchor and cantilever arms and their details were the subject of a great deal of study and of many tests. Little is known about bridge compression members when compared to tension eyebars. Ouebec compression chords are members of unusual size. only in work of great magnitude that the engineer has an opportunity to make tests on a large scale; the expense of such tests is trifling in comparison with the importance to the structure of the results obtained. It is not sufficient to know that in some bridges a compression member is still standing and is subjected to a certain stress. What we should know is how much greater stress it would take to destroy that member. Such a member may be in the stage of danger from the last straw. The board made a number of tests on models of chords and posts, both for the official design and for the final one. The tests gave generally better results for model members representing the latter. The board feels, therefore, that a good design for these heavy members has been obtained (Plate VI).

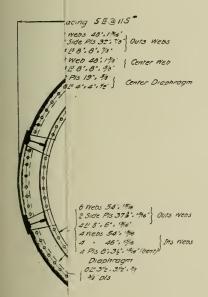
There never was any serious doubt among the members of the board as to the advisability of making the bottom chords of the anchor and cantilever arms riveted throughout without pin joints, except at the main pier bearings, to avoid excessive secondary stresses. This was done and will result in a stiffer bridge.

Top Chords.—The original design as submitted by the St. Lawrence Bridge Company contemplated top chords built of plates entirely. While this was approved at the time, later studies proved that by building the top chords of carbon steel eyebars there will be a slight saving of weight and cost, and the change was authorized. A tension member built of eyebars is the most reliable type by reason of the large number of full-size eyebar tests which have been and are constantly being made. It is the logical form of construction for transmission of tensile stresses. Their use reduces the secondary stresses. In a chord built up of wide plates with riveted joints, making it continuous, the secondary stresses resulting from bending due to the deflection of the span would be considerable, but owing to the uniform deflection of the "K" design they could easily be taken care of.

One of the guiding principles of the designers of the new

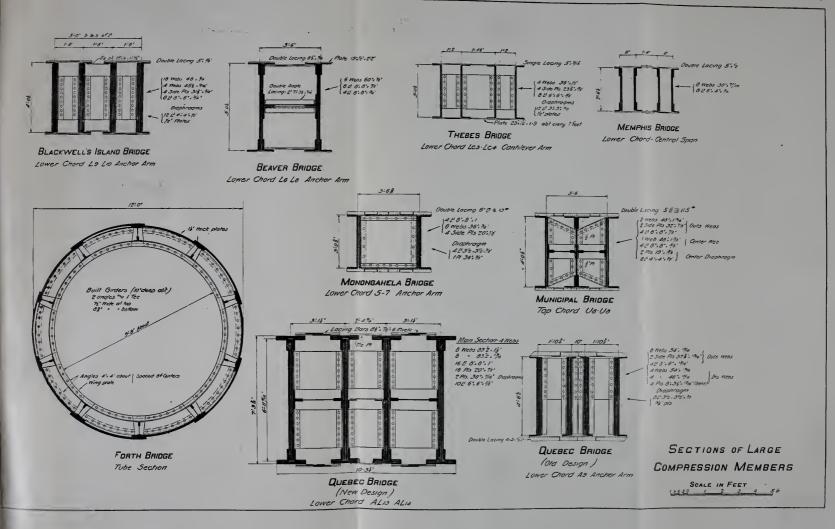


BLACKY Lower C



# SECTIONS OF LARGE COMPRESSION MEMBERS

Scale IN FEET -



Quebec Bridge was the elimination of untried features and experiments. In a span of this length some new features must necessarily be introduced, but they are limited to those only which grow out of the unprecedented length of span.

Suspension Bridges.—With the length of the Quebec span of 1800 feet and with the materials now at the disposal of the engineer, the practical limit of cantilever construction has very nearly been reached. In fact, if economy alone is to be considered, a cable suspension bridge would have been cheaper for a span of 1800 feet. The cantilever structure presents a greater rigidity under moving load, and this greater rigidity was the determining factor in the decision of the board to adhere to the cantilever type. Tentative plans of the suspension type with wire cables were, however, partly worked out by the board in the way of study.

The comparative rigidity of the cantilever system on one hand and the suspension type on the other may be gauged by the deflections at the centre of the span under full load.

New Quebec span, total live load	113/4 inches
A cable suspension bridge, trial design—live load only, over	2 feet
A cable suspension bridge—with 120° variation in temperature	
and full live load-between highest and lowest position	
about	7 feet

There are two reasons for the large deflections in suspension bridges: First, the deflection due to variations of temperature in the cables of a suspension span, which in a cantilever span is inappreciable; and, second, the fact that higher unit stresses are permissible in the wires of the cable than in the members of the cantilever span. The working unit stress in the wires is generally taken at from 55,000 to 60,000 pounds, while less than one-third of this is permissible in rolled carbon steel. When a moving load travels on a suspension bridge it subjects it to partial deflections which may be compared to a wave motion. This motion is greatly obviated by the use of deep stiffening trusses. The deeper those trusses are, the smaller will be the partial deflections. It is, therefore, an advantage to make these stiffening trusses as deep as practical considerations will permit. But, on the other hand, the deeper the truss the more equalizing will it perform and, therefore, the heavier will it

have to be. Each particular case must be studied in this respect, taking into consideration the relative importance of the live load which produces these local deflections, to the dead load. A suspension bridge generally consists of one main span and two side spans. There are two distinct types of side spans—one where these side spans are suspended from the cables, as in the Manhattan Bridge in New York (Fig. 24), and one where they are supported independently of the cables, as in the Williamsburg

Fig. 24.



Manhattan Bridge, New York. Showing type of suspension bridge with side spans supported from main cables.

Bridge in that city (Fig. 25). There are also two types of stiffening trusses for the main span—a continuous truss, as in the Manhattan Bridge, and a truss hinged at one or more points, as in the Brooklyn Bridge. For a bridge for highway and street car traffic, even though interurban trains are to use it, the most suitable type is the one with comparatively shallow stiffening girders continuous over the main span, with side spans suspended from the cables: this because of the absence of concentrated moving loads which would be heavy enough to cause appreciable local deflections. On the other hand, a bridge for railroad use, single-or double-track, should preferably be built with deep stiffening trusses over the centre span, hinged at centre or continuous, with

side spans supported independently of the cables. It is perfectly practicable to build an efficient and economical suspension bridge for railway use if these principles are adhered to.

The main parts of a suspension bridge are the cables. These are sometimes replaced by eyebar chains. The longest eyebar suspension bridge is in Budapest and has a span of 981 feet. The longest cable span is 1600 feet, and the one built by Roebling Brothers is still giving excellent service. There is no doubt, therefore, that the wire cable has been successful for long spans.

FIG. 25.



Williamsburg Bridge, New York. Showing type of suspension bridge with side span supported independently of main cables.

It is doubtful if an eyebar chain suspension bridge of 1800-foot span would prove economical as compared with the cantilever type unless some special steel with which we have had little experience be used. The impact from moving load in the chain would be within 10 per cent. of the impact produced in the top chords of the cantilever arms, so that much higher unit stresses in eyebar chain links than those used in eyebar top chords of the cantilevers would not be justified. The allowable working stress in cables is not less than 55,000 pounds per square inch, while it is not over 30,000 pounds in nickel-steel eyebars, or a little more than one-half.

From what was said throughout this paper it is obvious that

the longer the span the greater the need of materials of high resistance. For plate girders and short spans ordinary medium steel does very well and is used exclusively; for longer spans, beginning with 400 feet, alloy steel, such as nickel-steel, nickel chrome, vanadium, etc., may be used to advantage, this advantage increasing with the length of span. The practical limit of cantilever system for known materials is reached at about 2000 feet for a railroad bridge. For longer spans, suspension bridges should be used, and are made possible by the high resistance of wire cables. The practical span limit of a wire cable suspension bridge has been calculated at 4335 feet, assuming a working stress in the cables of 60,000 pounds per square inch.<sup>7</sup>

The breaking load of the cables was assumed at 180,000 pounds per square inch. If an alloy wire be used of a still higher resistance the practicable limit will exceed the one given above. The limit of length of a cable alone without any load except its own, stressed at 60,000 pounds per square inch, is 15,160 feet.<sup>7</sup> This assumes the versed sine of the cable to be ½.

An eyebar chain of alloy steel, such as now in use, should not be stressed beyond 30,000 pounds per square inch. Assuming this stress and a versed sine of ½8, the limit of length of such a chain will be 7010 feet. Hence, the limit of span length of an eyebar chain suspension bridge to carry live loads would be considerably below that of a cable suspension bridge.

The suspension design lends itself better to graceful treatment than a cantilever bridge, and may often be preferred for ornamental highway bridges even where a cantilever were to make a cheaper bridge.

Considering the purely utilitarian structures, such as the majority of railroad bridges, the present knowledge of metals and its alloys, and the present loadings, we may sum up the various types of large bridges as follows:

For spans up to 750 feet......Simple spans.

For spans from 650 feet to 2000 feet...Cantilever spans with suspended span. For spans from 1500 feet to 4000 feet...Cable suspension spans.

Arch spans have their place only where natural conditions are favorable, or for ornamental bridges.

<sup>&</sup>lt;sup>7</sup>Report of Board of Engineer Officers (U. S. Army) as to Maximum Span Practicable for Suspension Bridges, 1894.

Chain suspension bridges may be used for ornamental highway or city bridges, but for railroad service and for spans below 1500 feet the cantilever is to be preferred as giving a stiffer and generally a cheaper structure.

It will be noticed that the above limits overlap. Local conditions in each particular case will be considered in deciding whether a span between 650 feet and 750 feet should be simple or cantilever, or whether a span between 1500 and 2000 should be a cantilever or a suspension span.

Secondary Stresses.—I shall not dwell long on this latest addition to bridge calculations. That secondary stresses exist is a fact. They may be from three sources:

First.—Weight of member.

Second.—Temperature.

Third.—Bending from loads.

In the new Quebec design all secondary stresses were calculated and taken care of, but as a result of tests made by the Quebec Board, the stresses in tension members due to their own weight will be neglected. It is quite possible that if similar tests could be made for other secondary stresses it would be found that the metal adjusts itself to a large extent in such a manner as to reduce the importance of those secondary stresses and their influence on the elastic limit of the member. Personally, I feel there is a tendency at present to overrate the importance of secondary stresses. They should, of course, be considered in designing a structure; it should be the aim of the designer to reduce these secondary stresses to the minimum, but excessive refinement should be avoided, and unit stresses for direct loads should be made low enough to include these secondary stresses where they may exist.

Materials.—The proper selection of materials for a structure is an important part of the design. The ordinary commercial steel will do for rough plate girder work, but for large bridges a metal of higher quality should be used. The metal or alloy should have a high elastic limit, a high ultimate stress, and possess sufficient ductility, which is characterized by the elongation and the reduction of the cross-section of specimens tested, to allow its being worked in the shops without fear of injury. Here, perhaps, climatic conditions should be mentioned. Intense cold makes steel brittle. This is shown by the greatly-increased

number of rail fractures during severe winters. The use of high carbon steel should therefore be avoided in northern climates. The behavior of the various alloys in freezing weather needs yet to be studied.

In all that precedes I have endeavored to avoid speaking of matters which are usually given in text-books. I have also avoided mathematical deductions, leaving them to better mathematicians, and I have attempted to deal with this vast subject from a practical standpoint only. When the final report of the Quebec Board is published it will give in detail what I have merely been able to outline. Numerous most interesting tests and mathematical analyses have been made and will be published in the course of events. It will then, perhaps, be realized, even by the members of the engineering profession who had no opportunity to fully design a very long span, that, while it is very easy to draw a diagram and a few of the principal details. it takes months of study, of retracing one's steps, of tests and calculations to make a complete design and to learn that the preliminary diagrams and sketch details must often be changed entirely to make a practicable and an efficient structure.

Dynamics of the Electron. A. SIGNORINI. (N. Cimento, iv, Ser. 6, 257.)—This is an attempt to develop a mathematical theory of the motion of an electron in an electromagnetic field without subjecting the electron itself a priori to any kinematical linkage. The only distinctive property utilized is that its dimensions are infinitesimal with respect to those of the field. Following Larmor's mechanical conception, the electrons are considered as systems possessing a finite number of degrees of freedom. In the Lagrangian function of the mechanical model (excepting the connection between kinetic and potential energy) Abraham's assumption is made, in which only electrokinetic elements appear, such as the distribution of charges and currents, and retarded relative potentials. Levi-Civita's asymptotic expression is taken for the retarded potentials, and the previous history of the motion of the electron is thus eliminated. For any given position of the electron and for a given distribution of currents and charges the motion of the electron, which has 12 degrees freedom, is defined by a system of 12 ordinary scalar differential equation of the second order, in which the time appears as an independent variable.

## THE DIELECTRIC PROPERTIES OF NON-CONDUCTORS.<sup>1</sup>

BY

#### PHILLIPS THOMAS, Ph.D.,

Westinghouse Electric and Manufacturing Company.

This paper presents the results of an attempt to find some connection between the various electrical properties of certain insulating materials, and to secure evidence as to whether or not general relations hold between such properties of non-conductors as a class. The plan was to select, by preliminary tests, a few substances that differ greatly in specific inductive capacity, and to make extensive and accurate tests on the materials chosen. The data thus found were to be reduced to some form permitting ready inter-comparison.

The materials chosen for test were mica, paraffined paper, celluloid, and ice. The dielectric constants of these substances range from about 4 to about 100, when measured by alternating current of high frequency. The tests were made upon condensers having these materials as dielectrics, and were as follows:

- (1) Tests of capacity and power-factor at high frequencies.
- (2) Tests of insulation resistance by direct current, and of capacity on very short times of charge.
- (3) Tests of the breakdown strength of portions of the dielectrics, removed from the condensers.
- (4) Tests upon the change in capacity, due to varying the direct voltage applied to the condensers.

The condensers tested, with the exception of that in which ice was the dielectric, were parallel plate condensers of the ordinary type, and consisted of a number of sheets of dielectric, separated by sheets of conducting material, the whole being impregnated with paraffin and placed under pressure until the paraffin was nearly all crowded out. The mica condenser had not been so treated, however: in this case the leaves had been simply stacked without permanent compression and without paraffin.

<sup>&</sup>lt;sup>1</sup> Communicated by the author.

Each of the condensers had a fairly large capacity, that of all but the ice condenser being of the order of I microfarad. Because of this high capacity, and because of the large difference in power-factor between the standard condenser and the condensers tested, it was possible to use a simple modification of one of the Wien methods of measuring capacity and power-factor. The modification employed consisted in balancing the test condenser against an exceptionally good mica condenser. Adjustment to equality of power-factor was made, as a rule, by varying a resistance in parallel with the standard condenser: the resistance was used in series when the parallel value called for a very large resistance to effect a balance, as then the residual constants of the coils used became too large to be neglected.

The use of a Vreeland oscillator 2 made it unnecessary to correct the form-factor of the alternating voltage applied to the bridge circuit. Briefly described, this instrument causes resonating at its natural frequency to be continued indefinitely in a circuit containing a variable self-induction and a variable capacity. The exciting apparatus is a mercury vapor tube with two anode terminals, and the oscillating circuit is connected as a shunt to these two anodes, which form the common positive terminal of the direct-current mercury arc. The frequency of resonation may be varied by changing the capacity of the condenser, or by connecting the two reactive coils either in series or in parallel. The oscillating current is very approximately of true sine form. The self-induction and capacity in the oscillating circuit were measured, and had such values that the natural frequency, f, was given by the expression,

$$f = 1082 (c)^{\frac{1}{2}},$$

where c is expressed in microfarads, and the reactive coils are in series. The frequencies calculated by this expression were tested by connecting a telephone receiver to the terminals of a small coil of wire loosely coupled inductively with the oscillator circuit, and comparing the frequencies by the method of beats with those of a set of standard Koenig forks. The error made in these calculated frequencies was not more than I per cent.

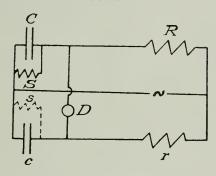
The complete theory of the Wien compensated bridge

<sup>&</sup>lt;sup>2</sup> Vreeland, *Phys. Rev.*, vol. 27, No. 4, 1908.

methods for the simultaneous measurement of the capacity and power-factor of condensers has been given by Grover.<sup>3</sup> When the capacities compared are large and have very different power-factors, the corrections for the small capacities and self-inductions in the measuring resistances will have a negligible effect upon the accuracy of the results.

The condenser used for the standard in all the tests was a Leeds & Northrup mica condenser, serial number 13.944. The condenser was supplied with a certificate from the Bureau of Standards which gave the power-factor as quite negligible for

Fig. 1.



the larger capacity values; the capacity change with frequency was also stated as extremely small. This condenser was compared with a large air condenser by the Wien method adapted for the regular tests, and it was found that the actual values of the resistances in the ratio arms of the bridge could be changed by more than 100 per cent. without effect upon the balance; also, that the power-factors of the mica condenser and the air condenser were so nearly equal that no series or parallel resistance was necessary to cause silence in the high-resistance watch-case telephone receiver used as a detector.

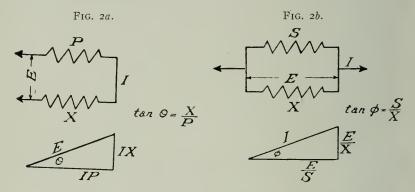
The standard condenser was assumed to have zero power-factor, and its capacity was assumed to be independent of frequency. In Fig. 1, C is this standard condenser, c is the condenser being compared with C, the ratio arms of the bridge are represented by R and r, the compensating resistance by S, and the fictitious parallel resistance of the condenser being tested

<sup>&</sup>lt;sup>3</sup> Grover, Bull. Bureau Standards, vol. 3, No. 3, 1910.

by s. When no current is passing through the detector, which is the condition of balance, the power-factor must be the same in both arms of the bridge, and the wave must have the same amplitude at each terminal of the detector D. From these conditions we have

$$c/C = R/r = S/s$$
.

The fact that condensers take some current when impressed with a direct voltage, over and above the capacity charging cur-



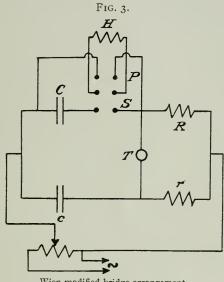
rent, led the writer to adopt the convention that the fictitious resistance is a resistance in parallel with the capacity. If a series resistance is used in place of S to compensate the bridge for power-factor, it is reduced to the equivalent parallel value by the equations obtained from Figs. 2A and 2B. If the two circuits there represented are equivalent,

$$tan\theta = tan\phi$$
, and  $PS = X^2$ ,

and the equivalent parallel resistance S can be calculated from the observed value of P. The actual bridge arms and the compensating resistances used were Leeds & Northrup dial type resistance boxes, and had the makers' guarantee of being accurate to better than 0.1 of 1 per cent.

The tests on all except the ice condenser were made at a temperature of 19° C. The condensers were kept in the test-room, which could be kept within 1 degree of this temperature by a thermostat. Condenser temperatures were read by mercury thermometers in intimate contact with the outer surface of the

condenser dielectric, and readings were recorded only when the thermometers had indicated the above temperature for some The connections used are shown in Fig. 3, where Rhours.



Wien modified bridge arrangement.

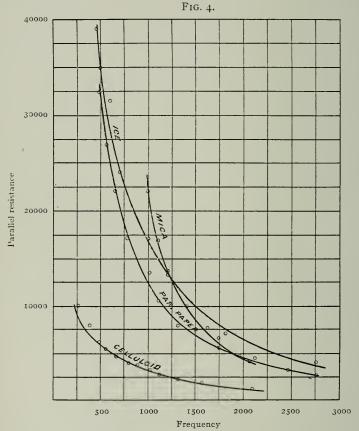
and r are the bridge arms, C and c the capacities, p the fictitious parallel resistance of the condenser c, and H the compensating resistance. When series values of H were used, which was

TABLE I. MICA CONDENSER. CONDENSER No. 13944 SET TO 0.5  $\mu$ . PERATURE 19.0° C. TEM-

f.	R.	r.	S.	c.	s.	х	p/x
966 1108 1206 1400 1726 2110 2748	804 803 803 803 803 802 801	1000 1000 1000 1000 1000	17800 13500 10700 7900 5200 3500 2100	0.402 0.4015 0.4015 0.4015 0.4015 0.4010 0.4005	22100 16800 13310 9840 6480 4370 2620	410 357 328 283 229 187 144	53.9 47.1 40.6 34.8 28.3 23.2 18.2

accomplished by throwing the switch to S, the values of S which occur in the equations and in the appended sample table of readings and calculated values (Table I) are found from the corresponding series values by the equation  $PS = X^2$ . In Table I, capitals refer to the standard condenser, small letters to the tested condenser.

To illustrate the method of recording data and calculating the constants of the condensers, the results obtained from the tests on the mica condenser are given in Table I. These results,

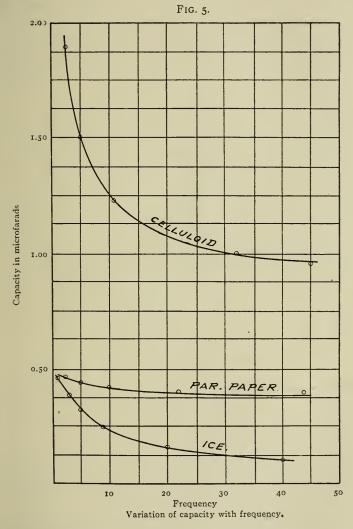


Variation of equivalent parallel resistance with frequency.

together with those of the capacity and power-factor tests on the other condensers, are plotted in Figs. 4, 5, 6, and 7. In the tests on ice, the capacity of c was much smaller than in the other tests, and the symmetry of the bridge was destroyed by the necessary employment of a long pair of air-insulated leads carried to the refrigerating room. The above method was there-

fore abandoned, and the tests were made by the following substitution method:

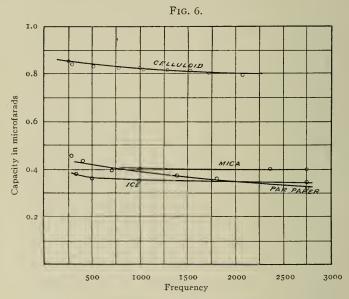
The condenser under test, and an auxiliary mica condenser,



were both placed at the end of the leads remote from the testing apparatus. The auxiliary mica condenser was first compared with the standard, and its capacity and fictitious parallel resistance calculated as indicated above. The ice condenser was then

Vol. CLXXVI, No. 1053-21

connected in parallel with the auxiliary condenser, and the combined condensers were compared with the standard, and the capacity and power-factor of the combination were similarly calculated from the results of this test. The ice condenser capacity was therefore the difference between the capacity of the combination and that of the auxiliary, while the equivalent parallel resistance of the ice condenser was found from the calculated parallel resistance of the combination and of the auxiliary

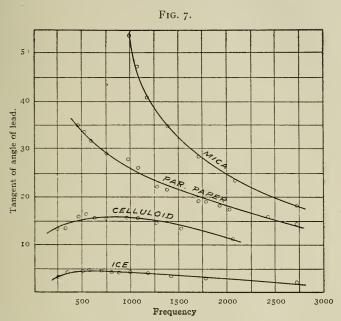


Variation of capacity with frequency. Scale of ordinates for ice is microfarads × 10-1.

condenser, just as one would calculate the second of two resistances in parallel, if the resistance of the first and that of the combination were known. The results found were thus independent of the capacity and resistance of the leads to the cold room. The ice condenser consisted of two brass cylinders, copper-plated from the same anode, and separated by ice frozen from water triply distilled. The dimensions of the cylinder of dielectric, when frozen, were: length, 42.0 cm. (16.55 inches); mean radius, 10.0 cm. (3.94 inches); thickness of dielectric, 0.30 cm. (0.18 inch). The water was frozen gradually from the bottom upward. Connections were made between the en-

closing metal cylinders and the testing bridge by a pair of bare copper wires. These passed through glass tubes where they pierced the walls of the building, and were suspended at but four other points.

The curves of Fig. 4, showing the variation of fictitious



Variation of tangent of angle of lead with frequency.

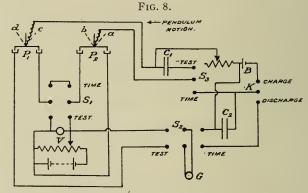
parallel resistance with frequency, closely resemble rectangular hyperbolas. An equation of the form

$$(f+a)(p+b)=k,$$

in which a, b, and k are constants determined from the curves, will give in each case values that agree closely with the corresponding points on the curves. It is improbable, however, that the relation is as simple as is indicated by this equation. It would be interesting to make further tests over an extended range of frequency; it seems probable that the equations calculated from the short range of frequency given in Fig. 4 would no longer hold.

To find the capacity of these condensers on times of charge

equivalent to frequencies lower than the lowest afforded by the Vreeland oscillator, a magnetically operated ballistic pendulum was used. This was constructed as follows: To the lower end of a long steel rod was attached a heavy bob of lead. This swung as a pendulum, and was provided with a polished pin bearing, which was supported upon an upright stand. On the lower end of the pendulum bob was a powerful electromagnet. The stand which supported the bearing of the pendulum also carried a brass sector, shaped to a radius from the centre of the pendulum bearing, so that the end of the iron core of the electromagnet



Connections for ballistic pendulum.

would just clear the sector when the pendulum was set swinging. On the sector were mounted two single-pole, double-throw switches, which made contact, when thrown from one side to the other, in mercury cups by means of fine platinum wires. Each switch carried a light armature of soft iron, and the pendulum, on passing this armature, would throw it over, thus effecting the desired circuit changes. The connections employed are given in Fig. 8. In this figure,  $P_1$  and  $P_2$  are the switches operated by the pendulum. The motion of the armatures is arrested, as soon as contact is made, by a steel screw in the armature coming against the metal of the mercury cup. The armatures were carefully adjusted to be free from any tendency to fly back after the pendulum had passed.

In testing a condenser for capacity, by this apparatus, the switches  $P_1$ ,  $P_2$  are thrown into the positions "a, c," and the circuit switches  $S_1$ ,  $S_2$ ,  $S_3$  are thrown into the "test" position.

The condenser  $C_1$  is thus short-circuited. The pendulum is then released with its electromagnet "on," and swings from right to left, throwing switch  $P_2$  to "b" position, which charges: the condenser  $C_1$  to the potential V. An instant later switch  $P_1$  is thrown by the pendulum to position "d," which disconnects the condenser  $C_1$  from the voltage and connects it to the galvanometer G, causing it to give a ballistic deflection, which is read. The electromagnet current is interrupted before the switches are reached by the pendulum in its return swing, in order to be sure that the charge has not lasted long enough for any appreciable amount to be absorbed, which would be shown by an apparent shift of zero of the galvanometer indicator. The galvanometer used, a Nalder Bros. D'Arsonval, was critically damped. Its proportionality on ballistic throws was tested over the range of deflection used in these tests, and was constant over this range to within 0.25 of 1 per cent. Its ballistic constant was  $5.77 \times 10^{-9}$  coulombs per scale division at a distance of 1000 scale divisions.

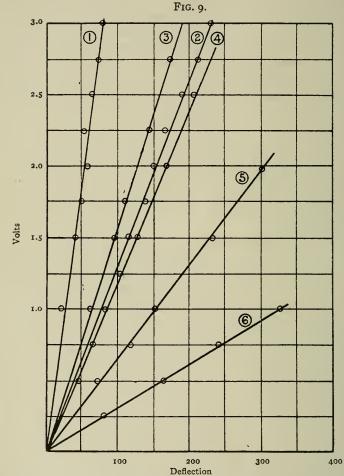
The time of charge of the condenser  $C_1$  is the time during which the switches  $P_1$ ,  $P_2$  are in positions "c," "b," respectively. This interval of time is measured as follows: Switches  $S_1$ ,  $S_2$ ,  $S_3$  are thrown into the "time" positions. By manipulating the key K, condenser  $C_2$  is charged to the potential B, and is immediately discharged into the galvanometer G, giving a ballistic deflection D. Condenser  $C_2$  is connected to the voltage B once more, then insulated; the pendulum is then released, and performs the same functions as in the "test" operation. This connects the resistance R across the condenser  $C_2$  for the time during which switches  $P_1$  and  $P_2$  are in positions "c" and "b." The condenser is discharged into the galvanometer by manipulating key K, before the pendulum reaches the switches in its return stroke, and this new deflection d, is read. This second deflection corresponds to the residual charge left in  $C_2$  after its contact with the resistance R. Then the desired time is given by the expression,

 $T = 2.3RC_2 \log_{10} D/d.$ 

For the best precision in the measurement of the time T, the resistance R was made approximately equal to  $T/C_2$ .

The ballistic pendulum could not be relied upon to give con-

sistently times of charge larger than 0.30 second or smaller than 0.0060 second. Remembering that the charging current through a condenser in each direction, on the application of alter-



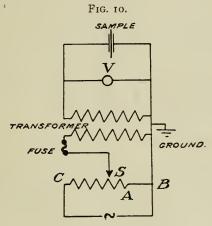
Voltage deflection curves for differing times of charging contact. No. 1, ice 0.025 second; 2, ice 0.35 second; 3, paper 0.008 second; 4, paper 0.19 second; 5, celluloid 0.011 second; 6, celluloid 0.19 second.

nating potential, continues through half a period, the frequency, f, is seen to correspond to a time of charge of  $\frac{1}{2}t$  seconds. It has been found that constants calculated by this relation from direct-current tests on condensers agree closely with those observed

with equivalent frequencies of alternating current. The frequencies used in plotting the curves in Fig. 9 are found from the measured times of charge by this relation.

The direct-current resistances of these condensers were found by the "leakage" method, using the pendulum as a charge and discharge key. The values found were reduced to specific resistances, and appear in Table IV.

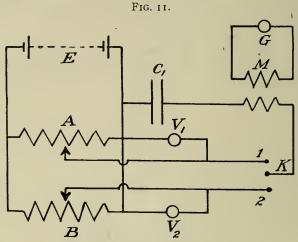
The breakdown tests were made upon portions of dielectric removed from the tested condensers. They were made as follows: The samples were inserted between highly polished discs



Connections for breakdown tests.

of brass, 2 cm. (0.4 inch) in diameter. The testing voltage was applied at a constant rate of about 600 volts per second. Fig. 10 gives the apparatus used, and the connections. The uniform gradient was secured by causing the slider S to move with uniform speed over the rheostat CAB. The speed had become constant by the time this slider reached A, having been started at B; and the portion BA of the rheostat was of negligible resistance. That from A to C was of such value that the transformer magnetizing current was about 1 per cent. of that taken by the rheostat, so that the voltage applied to the transformer, and hence that applied to the sample tested, was proportional to the distance AS. The breakdown voltage was read at the instant of breakdown on the electrostatic voltmeter V, which was

critically damped, and the speed of the slider S was the same as the free speed of the needle of the voltmeter V. The testing discs were polished after each test. In Table II the dielectric thicknesses appear in column "t." Column "E" gives the



Test for effect of voltage increase on capacity.

maximum corresponding to the (R.M.S.) reading of the voltmeter V at the instant of breakdown; and the quotient E/t, or the breakdown strength of I centimetre of dielectric between parallel faces, is given in column "P." This value holds only when

TABLE II. BREAKDOWN TESTS.

Dielectric.	t.	P.	
Mica Paraffined paper Celluloid	0.004 cm. 0.018 cm. 0.005 cm. 0.010 cm.	4,240 12,700 5,230 10,500	1.060×10 <sup>6</sup> 0.707×10 <sup>6</sup> 1.045×10 <sup>6</sup>
Ice	0.260 0.460 0.400	2,828 4,240 4,670	0.0106×10 <sup>f</sup>

testing terminals are used by which the field is not intensified at the boundary between terminal and air. In the case of ice, plane parallel plates were used, which had been frozen at the same time and from the same supply of water as the dielectric in the cylindrical condenser.

The fact that the curves of Fig. 9 are all straight lines shows that the capacity of these condensers was independent of applied voltage over the range of voltage used in the tests. The apparatus and connections used to test this point for higher voltages are shown in Fig. 11. In making a test, slider A was moved until  $V_1$  was zero, and switch K was thrown to position 1. Slider B was then moved until the voltmeter  $V_{\alpha}$  indicated a predetermined voltage which would cause a ballistic throw of G, just within the limits of its scale. K was then thrown to 2, the deflection noted, A was moved until  $V_1 = 2V_2$ , K was thrown back to position I and the new deflection noted, and so on up to the limit of the supply voltage E. The mutual induction coil M was used to get rid of the steady galvanometer deflection, proportional to the total voltage on the condenser, due to the condenser resistance. The results of these tests showed, when plotted in the form of curves, that the curve between voltage increment and galvanometer deflection was a straight line. The value of E was oo volts, and each condenser was taken through a cycle of from zero to go volts, back to zero, down to minus go, and back to zero. No evidence of any resulting closed loop was obtained.

The object of the work was to find any possible relation between the different electrical properties of the materials tested. To do this, the results are best shown as values per unit volume of dielectric, since the specific inductive capacities and the specific gravities are quite different. Table IV exhibits the final results of the work; and in order to make this table as clear as possible, the following explanation is given of the quantities tabulated, and their derivation.

Dielectric Constant, or Specific Inductive Capacity:

This was obtained by dividing the measured capacity of each condenser by the capacity of an air condenser of the same number of conducting sheets, the same average area per sheet, and an air separation equal to the thickness of dielectric in the condenser tested. If A is the product of the number of sheets by the average area per sheet, and t is the average thickness of one dielectric sheet, the capacity of the equivalent air condenser will be

The ice condenser had been used in some previous work,<sup>4</sup> and its air capacity had been directly measured. Table III shows the equivalent calculated air capacities for the four condensers tested. In Table IV the specific inductive capacity is the quotient of the measured capacity by the corresponding value of g from Table III.

TABLE III. CAPACITIES OF EQUIVALENT AIR CONDENSERS.

Condenser.	Air capacity, g. farads		
Mica. Paraffined paper. Celluloid.	$\begin{array}{cccc} 10.050 & 10^{-8} \\ 7.170 & 10^{-8} \\ 6.180 & 10^{-8} \\ 4.410 & 10^{-10} \end{array}$		

Maximum Breakdown Voltage per Centimetre. (See Table II.) Maximum Absorbable Energy, Watt-seconds per Centimetre Cube:

The energy required to charge a condenser c to a potential difference E is

$$Q = 0.5 cE^2$$
.

If the breakdown voltage per centimetre is represented by P = E/t, and if the condenser volume is V = At, where A is the total effective conducting area of one terminal, and t is the average dielectric thickness per sheet; and if K is the dielectric constant of the material, the condenser capacity will be

$$c = 10^{-13} A K/(1.132t),$$

provided that end effects may be neglected. Then the maximum amount of energy that unit volume of the dielectric can be made to absorb—regardless of the capacity which this volume of the dielectric is made to give—will be

$$W = 4.42 \times 10^{-14} KP^2$$
.

The limiting condition is that if a voltage be applied in excess of P, the condenser will break down.  $90^{\circ}$  Minus Angle of Lead:

The tangent of the angle of lead for a condenser is R/X, where R is the equivalent parallel resistance, and  $X = \frac{1}{2} \pi fc$ . The angle is calculated from the values of R, f, and c.

<sup>&</sup>lt;sup>4</sup> Thomas, Phys. Rev., vol. 31, No. 3, 1910.

Equivalent Parallel Resistance, Ohms per Centimetre Cube:

If the measured parallel resistance is R, the value per centimetre cube will be RA/t.

Conductivity per Centimetre Cube:

Reciprocal of equivalent parallel resistance.

Per Cent. Change in Capacity per Cycle:

If the capacity at frequency f is C, the per cent. change in capacity per cycle will be

#### 100dC/Cdf,

where dC and df are small corresponding changes in capacity and frequency.

Per Cent. Change in Equivalent Parallel Resistance per Cycle:

This is calculated from the curves, exactly as is the percentage change in capacity per cycle from the capacity curves. Direct-Current Conductivity per Centimetre Cube:

If D is the measured direct-current resistance of the condenser, the conductivity per centimetre cube will be

### $(DA/t)^{-1}$ .

It will be noted that in reducing the results to values for unit dielectric volume, the following assumptions were made:

- (1) That the breakdown strength of the material varies directly as the thickness between terminals.
- (2) That the power-factor, other things being equal, is independent of the value of the condenser capacity.
- (3) That the conducting area is very large compared to the thickness of each dielectric sheet.

In calculating the values which appear in Table IV, values for frequencies of 1000 and 15 cycles per second were deduced, as these are approximately the limits of commercial frequencies. The values given in Table IV show that there is a very evident general relation between the electrical properties of the four materials tested. As the dielectric is changed, from mica through paraffined paper and celluloid to ice, it is shown that the dielectric constants increase very greatly. At the same time, the breakdown strength becomes smaller, the resistance offered to the passage of both direct and alternating current grows less, the maximum energy that can be absorbed by a condenser of given dimensions diminishes, and the rate of change of capacity

with frequency increases; also, the alternating-current resistance of the material changes more and more slowly with frequency, which shows that a progressively larger percentage of the conductivity of the material is independent of frequency,—i.e., is a true "conductivity," and is not radically different on directcurrent and alternating-current circuits. It may be said here that the results found for mica are not necessarily valid, since

TABLE IV. RESULTS OF TESTS, AT UNIT AREA AND UNIT THICKNESS OF DIELECTRIC.

At 1000 cycles.	Mica.		Paper.		Celluloid.		Ice.	
Maximum breakdown volts per centimetre Specific inductive capacity Maximum absorbable energy, watt-seconds cm. cube 90°—angle of lead	1.06 4.00 0.198 0°-57 <sup>1</sup>	108	0.71 4.90 0.108 2-°101	108	1.05 13.26 0.640 3 -40 <sup>1</sup>	106	0.0004 0.0004	ļo
Equivalent resistance, ohms cm. cube Conductivity per centi- metre cube	2.56	10 <sup>10</sup>	1.02 9.84	1010	0.207		7.22	10 <sup>7</sup>
Per cent. change in capacity per cycle Per cent. change in resistance per cycle	2.18	10-4	14.31 0.146	0-4	30.7		70.0	10-4
At 15 cycles.								
Specific inductive capacity Maximum absorbable energy,  watt-seconds cm. cube			5.77		18.60		429.0	
Per cent. change in capacity per cycle	0.203		0.126		0.90		1.59	
On direct current.  Conductivity per centimetre cube	2.42	10-17	2.27	10-14	7.15	10-13	1.63	10-9

the only apparent difference between the standard and the tested condensers was in the method of manufacture. The diversity between the values found for mica and for paraffined paper, however, is far too great to be accounted for by differences in method of manufacture—and this is even more true in the case of the celluloid and ice condensers.

Grover (l. c.) has shown that the best possible single test on mica condensers is the power-factor test. It is evident from these results that in many cases the suitability of a given material for use as a condenser dielectric may be judged without recourse to a measurement of specific inductive capacity. The material covered in these tests, however, is not sufficient to warrant the conclusion that the relations indicated are of general application. An extension of these tests to liquid dielectrics would undoubtedly throw more light upon the point in question.

#### SUMMARY.

This paper describes and gives the results of tests upon the electrical properties of mica, paraffined paper, celluloid, and ice. The materials were tested in the form of condensers, and the tests included measurements of the capacity, power-factor, conductivity, breakdown strength, and capacity variation with applied voltage. The tests covered a range of from 3000 cycles to 250 cycles per second by sine-form alternating voltage, and from 83 cycles to 1 cycle per second by unidirectional charges applied for equivalent times of charge. The results of the tests were reduced to values for unit dielectric volume, and a table of such results is included. It is shown that there is a general relation between the electrical properties of the materials tested, i.e., that the substances with high dielectric constant have also high dielectric losses, low breakdown strength, and low insulation resistance. Temperature effects were eliminated by making all measurements on each condenser at a constant temperature. As far as possible, this temperature was made the same for different materials, so that a comparison of the results is not subject to temperature correction. It is shown that within ordinary commercial limits the capacity of condensers having either of these substances as dielectrics is independent of the magnitude of the voltage applied to them. The results of the tests are given in the form of curves.

In conclusion, the writer wishes to express his sincere thanks to Professors W. F. Magie and E. F. Northrup, of Princeton University, for their unfailing interest and invaluable assistance during the course of the work.

PALMER PHYSICAL LABORATORY, Princeton University, June, 1912.

Photography of Particles Ejected from Atoms. C. T. R. WILSON. (Engineering, xcv, 362.)—By the aid of Röntgen rays electrons may be ejected from ordinary atoms. Indirect methods are usually used in the study of electrons. Electrons, when ejected, left trails behind them, and these have been photographed. Each electron ejected traversed a large number of gas atoms. But on modern theories each such atom is a miniature solar system, the planets being represented by electrons, which are held together by electrical instead of gravitational forces. When a disturbance of sufficient violence was set up, an electron might escape from one system and might become attached to another system. Now molecules of gases or vapors would more readily attach themselves to charged ions than to uncharged atoms, and every ion could be made a centre of condensation in supersaturated water vapor. By the aid of the *cloud-chamber* the ions can be caught in the positions they occupy when just set free. The trail of a particle, invisible in itself, is thus marked by a crowded line of clouds, and individual ions could be distinguished under certain conditions. Nine photographs taken in this way are given in the paper, and three diagrams explanatory of the experimental methods adopted.

Photoelectric Behavior of Iron in Active and Passive State. H. S. Allen. (Roy. Soc. Proc., Ser. A, lxxxviii, 70.)—It is well known that ordinary iron which is acted on energetically by dilute nitric acid can be made to assume a passive condition by immersion in strong nitric acid or by other powerful oxidizing agents. The author has compared the photoelectric activity of iron in the active state with that of the same sample in the passive state, dry iron plates being used in each case. The photoelectric activity measured was that due to the light from a mercury lamp. The experiments prove that iron which is chemically active is active in the photoelectric sense, while iron which is passive shows much less photoelectric activity—in some cases none that can be detected. This result is considered in good agreement with the theory which attributes passivity to the condition of the gaseous layer at the surface of the metal.

Electric Locomotive for the New York Central Railway. Anon. (Elect. World, lxi, 797.)—In this article is given a detailed description of an electric locomotive, constructed by the General Electric Company. It has eight motors with a continuous, tractive effort of 10,000 pounds at 60 miles per hour. This locomotive weighs 100 tons, as compared with 115 tons, the weight of those already in use. It is more powerful than these, and is provided with forced air ventilation with a view to continuous high-speed service.

#### THE RELATION OF MATTER TO ELECTRICITY.\*

BY

## ARTHUR WILLIS GOODSPEED, Ph.D.,

Professor of Physics, University of Pennsylvania.

Member of the Institute.

In my address this evening I am prepared to outline in simple language the present attitude of science toward electricity and its relation to matter. It will, of course, be quite impossible in the time at my disposal to give the lines of reasoning or the methods of investigation which have led up to the present-day conclusions very generally accepted. Those wishing to study the subject more in detail, I must refer to the original papers of the several experimenters to be hereafter mentioned, whose work furnishes strong evidence in favor of the views here to be set forth.

My discourse will not be ultra-scientific, but I shall try to give the layman an intelligent notion of what science has done and is doing in this special line of investigation.

We live in a wonderful age-not only relatively but absolutely, and I refer not only to the marvelous progress in pure science, but to the most impressive results due to the successful applications of the principles of pure science to the production of useful appliances. Within my own recollection have appeared the invention of the telephone and its adoption by the whole civilized world—the application of electricity to not only local motive power, but also to that of moving vehicles of all kinds. even the most powerful locomotives for drawing the fastest passenger trains—the internal explosive engine used on a large percentage of the automobiles now made—the useful development of the electromagnetic theory of light from the mathematics of Maxwell through the experimental demonstration of Hertz to the application by Marconi and others for the purpose of signalling at a distance without the use of any conducting wires. These and many other things could easily be enumerated to

<sup>\*</sup> Presented at the meeting of the Section of Physics and Chemistry, held Thursday, March 6, 1913.

illustrate the wonderful progress of physical science and its applications during the last twenty-five years, and to treat any single one in any detail would require volumes rather than the few pages devoted to the present discourse.

As the recent progress of the science of electricity and its industrial applications has perhaps been the most remarkable and contributed most to the welfare of mankind, it is quite fitting that we should consider briefly the nature of the agent which is directly or indirectly responsible for the effects produced, and determine if possible what relation it bears to the other agencies or entities with the nature of which we feel more familiar.

Not so very long ago teachers of physics used boldly to assert that matter and energy comprise every conceivable existence in the physical world. Electricity and the ether, however, presented difficulties to this brief classification, though it was often predicted that at some time and somehow electricity would be shown to be a connecting link between ether and matter. Although this expectation has not been up to the present time realized, the accepted belief as to the relation of electricity to matter will be apparent when we have taken a brief survey of the evidence about to be presented.

Since I have referred to the ether it seems fitting that a brief comment should be made in regard to it. As the wave theory of light more than a hundred years ago gained ground against the corpuscular theory long held by Newton and his followers, it became necessary to postulate a medium in which the waves could be propagated. The necessary properties of such a medium to account for the special kind of wave and their high speed were listed and described. The belief in the existence of some sort of medium seemed imperative. For example, heat and light are present in the sun; 8 minutes later they are received by the earth; during that 8 minutes where are they and what are they? "Radiant energy in the ether," has been the universally accepted answer till quite recently, and the postulate of the ether has been one of the fundamentals of physics. Even up to 1904. at the Congress of Arts and Science at St. Louis, physics was discussed under three heads, as "physics of matter," "physics of the ether," and "physics of the electron." Even at the present time, I believe that the great English physicist, Sir Oliver Lodge,

contends that the ether has a very definite and concrete reality. On the other hand, within the last few years there has been developed a new branch of philosophical physics, known as "The Principle of Relativity," enunciated by Einstein of Berne and mathematically studied by Minkowski. In America the chief writers have been Lewis, Comstock, and Tolman.

The theory of relativity is an attempt to furnish a logical explanation of two experiments on the velocity of light, the results of which at first seem contradictory. We have not time to consider these experiments, but one of them was by Fizeau. in 1851, which seemed to show that the properties of the ether through which light passes are in no way affected by the motion of a gas present; i.e., the ether stays at rest. If this be so, the velocity of light should be different, depending on the direction of the observer with reference to the light source. Michelson and Morley tried this test with the greatest care, using methods sure to detect a difference if it existed. None was found. In other words, the ether has not been proved to be at rest relatively to moving matter, and the relativists are inclined to conclude from this that no such medium as the ether really exists and that we are just as ignorant of the mechanism of the transmission of radiation as we are of that of gravitation. So physics along these lines may be on the verge of another revolution, though the speaker is inclined for the present to retain his mental conception of an elastic ether and its electromagnetic waves.

The objectivity of matter, I presume, is apparent to all of us, Tait calling attention to the fact that it is often offered "for sale" or "for let," and, of course, anything that can be bought or hired must have an objective existence. But surely accepting such an argument would imply far too much now in America. Indeed, the same author admits later that "to have its price" is not conclusive of objectivity, citing as evidence that titles, family secrets, and even college degrees are sometimes sold.

On first thought it would seem far easier to study matter than to study energy, and this is so, perhaps, if one does not proceed farther than to analyze and to classify the properties of the bodies having tangible and visible size. We can, for example, find out nearly all there is to know about a certain piece of glass, considered only as a mass of glass of definite size and shape.

Vol. CLXXVI, No. 1053-22

We can measure its mass correct to one part in ten million; its linear dimensions correct to one-hundred-thousandth of a centimetre; its density, elasticity, refractive index, dispersive power, etc., are known to a high degree of accuracy. Suppose now we have made a similar physical examination of a definite piece of quartz; at once is suggested, why this difference in properties? They must be due to the differences in the finer structure of the substances not apparent by the grosser methods of examination. Chemistry now steps in with its beautiful analytic methods and classifies the many substances or kinds of matter composing bodies.

At any particular time in the history of science a chemist would have told us that all substances are either elementary or compound, the number of the former class being definite, say seventy-five, while the number of compounds is far greater and less definite. At almost any subsequent date the number of elements would be stated as larger, this increase from time to time resulting in the dividing of a supposed element into two, or, from the discovery of new ones, all the former ones remaining intact. The separation of didymium a few years ago into its neo- and praseo- constituents is an example of the former method, while the latter has been exemplified more recently by the discovery of several unsuspected constituents of the atmosphere—I refer to the inert gases of the argon group.

Until rather recent years physics was said to treat of masses and of molecules and their energy relations, while chemistry investigated molecules and atoms and their energy relations. More recently physics and chemistry together, aided by that ever-powerful ally, mathematics, have strenuously attacked the atom, hoping through this doorway—narrow, it is true, but manifold—to flash now and then a ray of light illuminating for a moment, if but dimly, the mysteries beyond.

I have used the terms molecule and atom. Let us note clearly what these signify. The former, which from its derivation means "a little mass," is defined as the smallest portion of any particular substance or kind of matter which can exhibit the properties of that substance. For example, the smallest particle of common salt that is salt is the molecule; if by any means, as in chemistry, we subdivide the molecule, we get atoms,

alike or different, and these present properties entirely different from those of the molecule. In the case cited a molecule of salt is built up of an atom of the metal sodium and an atom of the gas chlorine—two substances quite unlike and each entirely different from salt. These are called elements. The suggestion of an atomic theory of matter is over two thousand years old, but the real founder of the scientific modern kinetic theory was the English chemist Dalton, and during the last century it has been established upon a most firm foundation.

Suppose we consider for a moment the size of these atoms of which we so confidently speak. Chemistry furnishes us with indisputable evidence as to their *relative* sizes; we know that an oxygen atom is about sixteen times as massive as one of hydrogen, which is the smallest known; but what about actual size? I cannot give you the methods of attacking this problem; many there are, but I can briefly state the results.

In describing magnitudes of quite different orders we are forced to adopt appropriate units for expression that the mind may, in a measure at least, be able to appreciate the different magnitudes expressed. The mention of a mile calls to one's mind a rather definite length which it appreciates, so when one is told that two places are twenty-five miles apart we know about what that means. If, however, this distance were expressed in feet or in inches, no one would have any idea of the magnitude expressed, because of the inappropriateness of the small unit to express so large a distance. Again, we receive very definite information when told that two stakes are placed ten feet apart, while if this distance were expressed in miles we should again be hopelessly confused.

Now a molecule is so small at to require an exceedingly small unit to express its size. Microscopes with their micrometre eyepieces can measure distances smaller than a one-hundred-thousandth part of an inch, or about one-half the wave-length of yellow light. But this distance is one thousand times greater than the probable diameter of a hydrogen atom. A better idea is gained in this way than if I had said at first that the diameter of a hydrogen atom is about a hundred-millionth of an inch. Again, as you all know, nearly all scientific measurements are made in the metric system, in which a metre (about 40 inches)

is the starting point. A thousandth of this is a millimetre (about 1/25 inch), and a thousandth of this is called a micron, and 4000 hydrogen atoms laid side by side would reach about this distance. Further, it is estimated that the number of atoms in a single drop of water would be expressed by a number far beyond one's mental power to appreciate—a number requiring twenty-two or more figures to write.

Again, the kinetic theory of matter now universally accepted teaches us that these atoms and molecules are in a state of ceaseless motion, the energy of which constitutes heat. The conditions are simplest and best understood in the case of a gas such as the air. If we imagine air magnified about a thousand million times, to use an illustration of Millikan's,—i.e., to make a pea grow to the size of the earth,—a molecule would be about as large as a football, and if we could get an instantaneous snapview of the situation the scattered state of these bodies would be represented by one football in each ten-foot cube. Furthermore, the state of motion would be such that on the average each would travel about 300 feet before hitting a fellow. Furthermore, in the case of hydrogen, the molecular speeds are of the order of magnitude of a mile a second.

The advances in physical science during the last century have been many and rapid, yet made with such care, each new discovery or generalization being criticised so severely and impartially, that what has stood all tests and finally been generally accepted forms a most stable and reliant structure, to which, very recently, the trial framework of another story has been erected.

From the various experiments described by Crookes in 1879 he was led to believe that the residual gas in a very highly exhausted glass bulb when subjected to the action of an electric discharge from an ordinary induction coil presents properties so different from those of ordinary gas as to warrant the use of the term "radiant matter" to what we now call the cathode rays, and a more appropriate term cannot be conceived of in view of later researches. Crookes himself believed these to consist of streams of negatively electrified molecules projected with high speed from the cathode, and he constructed a number of ingenious mechanical devices in support of this view. Al-

though Crookes's conclusions were not then accepted by all, later developments have shown them to be in the main correct, except as to the size of the particles concerned.

It had been shown by Crookes that the cathode stream is easily deviated, both by a magnetic field and by an electrical one, and so by an ingenious though simple line of reasoning, based upon well-known principles of dynamics, J. J. Thomson was able to determine the speed, the mass, and the electric charge of these little bodies. It was found further that the results were quite independent of the residual gas in the tube and also of the material of the electrodes. As we proceed this will be seen to be very significant.

The reasoning and the mathematics, though simple, would be out of place in an address of this character, and I must ask you to accept the results. In Thomson's experiments the values obtained for v, the speed of the particles, was between 2.2 and 3.6 times  $10^9$  cm. per second, or about one-tenth that of light, the latter being  $3 \times 10^{10}$  cm. per second.

The value of e/m or of the ratio of the electric charge to the mass of its carrier was found to be between 1.5 and 2.0 x  $10^7$ , each being measured in c.g.s. units. It was further found that this value also is quite independent of the kind of gas filling the tube before exhaustion, and also of the substance composing the electrodes. Thus one is forced to the conclusion that these little carriers, or "corpuscles," as Thomson called them, must be quite a strange form of matter and not at all identical with either a molecule or an atom, though perhaps forming a part, always the same in character, of atoms of all kinds.

Now it has further been shown that the value of c, or the charge conveyed by each carrier, is the same as that carried by a hydrogen atom in liquid electrolysis and therefore since about  $10^{-4}$  of a gramme of hydrogen carries a unit charge, it follows that each corpuscle must have a mass equal to from one-fifteen-hundredth to one-two-thousandth of that of a hydrogen atom. In other words, the atom of the chemist and of the physicist, conceived of more than two thousand years ago by Democritus, and glorified, as Tait puts it, in that grand poem of Lucretius; of the chemist as the smallest portion of matter capable of forming part of a compound substance, of the physicist as the smallest

part that can receive or give an impulse or take part in an energy change, has been shown in the last few years to be about 1760 times more massive than the little body under discussion, and this even though we choose the least atom known, that of hydrogen.

In 1895 Röntgen discovered some very wonderful radiant effects from a Crookes tube, called by him the X-rays, the properties of which have been studied ever since all over the world, and which have become of vital importance in several departments of science. They differ from cathode rays in not being deviable by either a magnetic or by an electrical field. They are unlike light rays in not being susceptible either of reflection, refraction, or polarization within the usual meanings of these terms.

About a year after the Röntgen rays were discovered other rays having some properties in common with them and with the cathode rays also were discovered by Becquerel to be given off by uranium and its compounds. The results of the study of these rays have led to the development of a new subject in physics—radioactivity. A radioactive substance like uranium or thorium and their compounds is one giving off rays material or other kinds capable of ionizing the air, *i.e.*, making it a conductor of electricity.

Suppose we have a gas between two metal plates attached each to a terminal of some electric generator so that one plate is, as we call it, electrified positively and the other negatively. Ordinarily a state of equilibrium is maintained, as the gas is a first-rate insulator and no current passes between the plates. If. however, a uranium or a thorium compound be placed between the plates, the gas at once becomes partially conducting,—i.e., it is said to become ionized,-and a small current begins to flow, which can be measured by suitable devices. It is this ability to ionize a gas that makes it possible to study radioactivity. Except at very low pressures it is thought that an ion consists of a charged nucleus surrounded by an attached group of atoms. At very low pressure the negative ion is identical with a particle in the cathode stream of a Crookes tube. Conduction in the gas thus consists of the carrying of the negative charges by the ions to the positive plate and of the positive charges to the negative plate, thus tending to equalize the potentials. We have here then true electric convection.

In 1898 Mme. Curie, having taken up the study of the various salts of uranium and then of the various minerals containing uranium, announced through Professor Becquerel her results. Her first important conclusions were that the salts were active in proportion to the uranium in them, but that the minerals were not so. For example, uraninite, or pitchblende, as it is called, was found to be several times as active as metallic uranium itself, hence uranium cannot be the chief agent in the production of the effects in the case of the ore.

After a long and most careful chemical research Mme. Curie and her husband separated from a very large amount of uraninite a very small quantity of an active substance similar to bismuth which seemed to be a new element. They called this polonium, from Poland, their native country.

Continuing their work with vigor, the Curies soon announced the separation of still another elementary substance from uraninite closely allied to barium with a radioactivity many thousand times that of metallic uranium. This they called radium. The great popular as well as scientific interest in this wonderful substance would justify the time necessary to relate some of its properties, even if it did not furnish a very suitable example for illustrating the latest theory of matter, to be spoken of presently. The quantity of radium obtainable from uraninite, so far the most fruitful source, is exceedingly small. It is estimated that to obtain a single pound, and that far from pure, would require the working up of 2000 tons of the mineral.

A third radioactive substance, which is allied to iron, was discovered by Debierne in 1899; this he called actinium. These events opened up an entirely new department of science, and the superb research work of the Curies, J. J. Thomson, Rutherford, Kaufman, Boltwood, Millikan, and many others probably whose names should with equal justice be mentioned, has resulted in much new science and in throwing some light on the mysterious problems yet to be solved.

Without going into the details of the methods of investigation, let me say briefly that it has been found that radium, for example, sends out so-called "rays" of three kinds. Rutherford designated them, first the a-rays, which were found to be positively electrified particles penetrating ordinary matter but feebly,

only very slightly deviable in the strongest force fields, and having a mass of the same order of magnitude as that of hydrogen atoms; second, the  $\beta$ -rays, identical with the Crookes or cathode rays,—i.e., negatively charged particles, very penetrating, easily deflected by both a magnetic field and an electrical one, called at first "corpuscles," but later identified with electrons or the ultimate building material of atoms; and, lastly, γ-rays, probably identical with the Röntgen rays, very penetrating and non-deviable. A detailed study of radioactive phenomena shows with little doubt that the process is absolutely unaffected by any physical or chemical treatment. The activity is unchanged in passing from the temperature of liquid air to that of red heat. The activity of a radium compound is in direct proportion to the amount of uranium present, and is in no way dependent on the other substances in chemical composition. It would seem. therefore, that the changes going on are associated only with the atom of the active substance and not at all with the molecule of which that atom is a part. Since, too, it is only a substance of the greatest atomic mass, as for example uranium and thorium, which is radioactive, it is clear that the expulsion of a few a-particles would be quite possible without changing very much the total mass of the atom. For example, uranium changes its atom by the expulsion of two a-particles to a new and different atom discovered by Boltwood and named by him ionium, while ionium changes to radium by the loss of another a-particle. The proportion of the total atoms present at any time which expel a-particle each second differs with the different substances. For instance, the substance into which radium changes is a radioactive gas first known as radium emanation and later called niton; of this substance about two-millionths of the total number of atoms present at any time change per second. The result of this is that a given amount of niton is half changed in about 3.75 days. This is a rather rapid change, radium being reduced to half value in about two thousand years and uranium in  $4.6 \times 10^9$  years. The view that the atoms of the radio-elements are undergoing spontaneous disintegration was put forward by Rutherford and Soddy as a result of evidence of the character cited above. On this view it seems probable that the escaping  $\alpha$ - and  $\beta$ -particles are not set suddenly in motion, but that they

escape from an atomic system in which they were already in rapid oscillatory or orbital motion. The energy is then not communicated to the projected particles, but exists beforehand in the atoms from which they escape.

We have spoken of the  $\beta$ -particles as the electrons, but what about the a-particles? It was early shown that these are identical from whatever source derived, and, further, that helium is always associated with the minerals containing radioactive substances. This suggests that it has some necessary connection with the radioactive process. Helium has a peculiarly interesting scientific history. It will be recalled that in the early study of the spectrum of the sun a prominent line in the yellow close to the sodium lines was noticed by Lockyer which could not be identified as caused by any substance known then on the earth. The substance in the sun giving rise to this line was appropriately More recently, in 1895, Ramsay discovered named helium. helium occluded in certain minerals, notably cleveite, which were soon found to be radioactive. A little later Ramsay and Soddy obtained the helium spectrum from the gas emitted from a few milligrammes of pure radium bromide dissolved in water. The crucial test, proving beyond a reasonable doubt that a-particles without their positive charges constitute the helium atoms, was made by Rutherford by direct experiment, and Rutherford and Boltwood have made the latest and the most complete series of experiments for the direct determination of the amount of helium produced from a given quantity of radium under given conditions. Helium is further noted in being the most difficult and hence the last gas to be liquefied. This difficult feat was at last accomplished by Onnes of Leyden. At atmospheric pressure helium liquefies at 4.26° absolute; its critical temperature is 5.25° absolute and its critical pressure 2.26 atmospheres. When boiled at reduced pressure a temperature of about 1.5° absolute results, the lowest yet obtained.

Let us now return to the  $\beta$ -particles which have been shown to be identical with the cathode rays in a Crookes tube, except that when emitted from radio-atoms their speed is much greater, sometimes reaching nine-tenths that of light.

Since an electrically-charged body exerts force all around itself, it can be shown from theoretical considerations that to

start or stop or to accelerate such a mass requires a greater force than when not charged; this means that the body's inertia, or effective mass, is greater when charged. This is clearly due to the effect of the magnetic field always present when electricity is in motion.

In symbols, if the simple dynamic mass energy is  $\frac{1}{2}m v^2$ , m being the mass and v the speed, it has been shown by J. J. Thomson and others that this extra work required to produce the magnetic field is

$$\frac{1}{3} \frac{e^2}{a} v^2$$

where e is the electric charge and a the radius of the charged sphere.

Adding the magnetic energy thus developed in the ether to the mass energy, the total becomes,

$$E = \frac{\mathbf{I}}{2} \left( m + \frac{2}{3} \frac{e^2}{a} \right) v^2$$

in which the quantity in parentheses becomes the effective mass or the real inertia of the combination, and

$$\frac{2}{3}\frac{e^2}{a}$$
 the electric inertia.

Now let us take quite another attitude and adopt Faraday's conception of tubes of force and endow these tubes with momentum. Assuming again the same conditions, we can prove mathematically that the electric momentum due to the moving charge e—would be

$$\frac{2}{3} \frac{e^2}{a} v,$$

which gives the same value as before for the electric inertia,

viz., 
$$\frac{2}{3} \frac{e^2}{a}.$$

Mental help can be derived in thinking of these phenomena by noting the sensation experienced in pulling a body through a limpid liquid like water. Mathematical analysis proves that the apparent inertia of a sphere is increased by one-half the

liquid mass displaced. This effect in the case of a sphere is independent of direction of the motion, because of the symmetry of the spherical form. If, however, a long cylinder be propelled in a liquid, the external inertia will clearly be dependent on the direction of the motion relative to the longest or shortest dimensions of the cylinder. If the motion be parallel to the axis of the cylinder, a small liquid displacement per unit distance of motion will result; while if the movement be at right angles to the axis, the maximum external inertia is experienced. Furthermore, if an infinite cylinder in a liquid (e.g., a tube of force in the ether) be moved in any direction (except longitudinally, which means that it is not moved at all), it has external momentum only at right angles to its length. The energy of a tube we conceive as belonging to the body from which the tube originates, the inertia being due to the grip of these force tubes on the ether (to use an expression of J. J. Thomson).

In the discussion resulting in the conclusion that the electrical mass of a charged body in motion is proportional to  $\frac{e^2}{a}$  the speed was supposed small in comparison to that of ether wavemotion, or the velocity of light.

In the case of an electron having a velocity of the same order of magnitude as that of light, as does a  $\beta$ -particle from a radioatom, a further analysis is necessary. In this case the electrical mass will depend on the speed. A contemplation of Doeppler's principle will make this evident, since, as the charge changes position, there is a continuous though not instantaneous readjustment of the lines of force, which would radiate in all directions in straight paths if the charge were at rest. When the speed of the charged sphere has reached that of ether wavemotion the force tubes would all be equatorial and the inertia infinite.

If, then, it could be shown experimentally that the effective mass of a moving charged body is dependent on its speed, a part at least of this mass would have to be electrical, and due to this force-tube inertia. The experimental test of the question was made by Kaufmann when he measured the ratio  $\binom{e}{m}$  in the case of the fast moving  $\beta$ -rays from radium. These rays have a higher average speed than cathode rays, and in Kauf-

mann's experiments rays of different speed were measured. The ratio  $\left(\frac{e}{m}\right)$  varied from (1.31 to 0.63)  $\times$  10<sup>7</sup>, according to the speed of the particles.

Various formulas expressing the variation of mass with speed have been developed by J. J. Thomson, Heaviside, Searle, and others. To interpret his results Kaufmann used a formula developed by Abraham, as follows:

$$\frac{m}{m_0} = \frac{3}{4} \quad \frac{\mathrm{I}}{B^2} \left[ \frac{\mathrm{I} + B^2}{2B} \log \frac{\mathrm{I} + B}{\mathrm{I} - B} - \mathrm{I} \right],$$

in which

 $m_0$  = mass of electron for slow speeds, m = its mass at any speed,

 $B = \frac{v}{V}$ , where v is the speed of the electron and v that of light.

Referring now to Kaufmann's experimental results mentioned above, attention is directed to the following table:

I	II	III	IV
υ	$\left(\frac{e}{m}\right)$	$\frac{m}{m_0}$ (Exp.)	$\frac{m}{m_0}$ (theory)
2.36 × 10 <sup>10</sup> 2.48 " 2.59 " 2.72 " 2.83 "	1.31 × 10 <sup>7</sup> 1.17 " 0.97 " 0.77 " 0.63 "	1.50 1.66 2.00 2.42 3.10	1.65 1.83 2.04 2.43 3.09

Column I gives five speed values actually measured of  $\beta$ -rays from radium. Column III gives the corresponding  $\left(\frac{e}{m}\right)$  for each experiment. Column III gives the five respective values calculated from the results of experiment, of the ratio of the mass of radium  $\beta$ -particles to that of slow-moving electrons. For these letter particles  $\left(\frac{e}{m_0}\right) = 1.95 \times 10^7$ , the speed being comparatively slow, the charges being, of course, the same. In Column IV are found the ratios of the same masses calculated from the theoretical formula by substituting the different values of v given in Column I. Attention is called to the very close agreement be-

tween Columns III and IV, and also to the very weighty evidence thereby offered that the *total* mass of a moving corpuscle is electrical. It is surely worthy of note, too, that the agreement is closer for the higher speeds, which further strengthens one's belief in the theory that all the mass of an electron is electrical.

During the last year or two Professor Millikan,<sup>2</sup> of the University of Chicago, has made some very remarkable experiments tending to prove beyond possible question not only the truth of the kinetic theory of matter but the atomic nature of electricity. A further purpose of Millikan's work was to determine the most probable value of the electron, or one atom of negative electricity, in c.g.s. electrostatic units. He was able by observing the motions of electrified microscopic oil drops balanced against gravity in an electrical field, variable at will, to calculate the value of the electron to a high degree of accuracy. This value is said to be  $(4.771\pm0.009)\times10^{-10}$ .

In the preceding discussion it has been assumed that electricity is only of one kind, this being the kind conventionally called negative. On this hypothesis an uncharged neutral molecule becomes negatively charged by the acquisition of an extra electron, and positively charged by the loss of one.

It will be remembered that the old two-fluid theory of electricity assumed three entities, positive electricity, negative electricity, and matter—uncharged matter having combined within it equal quantities of positive and negative electricity.

The one-fluid theory of Franklin assumed the existence of two entities, matter and positive electricity, the former in a neutral state having combined with it a certain normal quantity of the latter. A positively charged body was then one having more electricity than normal, and a negatively charged one had less.

The present theory assumes only one entity, the kind of electricity formerly called negative, atoms of matter being made up of different numbers and arrangements of these smaller atoms of negative electricity or electrons.

The following crude illustration may help to make this idea conceivable: For example, a whole city (a molecule) or group of cities (a mass) might be composed of separate buildings (the

<sup>&</sup>lt;sup>2</sup> Popular Science Monthly, April, 1912.

atoms), either all alike (an element) or of many shapes and sizes (a compound), while every building might be made of bricks (the electrons) exactly alike in every respect. This notion that all matter in its simplest state is of only a single kind is, of course, not new, though the very forcible experimental evidence indicating such a state of affairs and that this ultimate unit of structural material is the atom of negative electricity has been offered within a comparatively short time. While it may be urged that another step has indeed been taken, but only deeper, into the mystery, yet, assuming the truth of the above conclusion, we find ourselves now face to face with a single problem instead of many, the solution of which would open wide the door to a comprehensive knowledge of many things now unknown and formerly unknowable.

The Acetylene-Electric Flame. C. F. LORENTZ. (Electric World, lxi, 511.)—When a powerful electric field is applied at right angles to a gas flame, the flame is deflected toward the cathode. There is no deflection until the anode is inside the invisible vapor mantle surounding the flame, and the deflection is accompanied by a small current through the flame. The deflection is due to the greater potential drop at the cathode, due to the greater mobility of the negative carriers. If a heavy current is passed, the action at the cathode is confined to one spot, which is heated sufficiently to emit ions copiously, and then the deflection ceases. If an arc discharge is passed at right angles to a flame carrying a large proportion of free carbon, there is a great increase in the luminosity of the flame. Acetylene is found to be a convenient illuminant, and curves are given showing the increased candle-power and the watts consumed. Direct current is more efficient than alternating, but the watt consumption for the increased candle-power is high. It is suggested that this type of flame is an efficient source of ultraviolet light.

Mortars and Concretes. H. Burchartz. (Mitt. Kgl. Materials, prüfungsamt, xxxi, 80.)—The addition of trass slightly retards the setting of mortars and concretes, increases their resistance to water, greatly increases the strength of mixtures gauged with lime-water, and decreases the detrimental effect of soap solution. Lime-water increases the strength of trass mortars, but has no influence on the strength and water-tightness of mixtures which do not contain trass. Soap solution renders mortars and concretes water-tight and diminishes the hardening of mortars without trass, which weakening effect is counteracted by the addition of trass.

## COLLOIDS AND CRYSTALS, THE TWO WORLDS OF MATTER.\*

BY

#### ROBERT H. BRADBURY,

Head of the Department of Science in the Southern High School, Philadelphia.

Member of the Institute.

T.

When a solid is brought into contact with a liquid the result depends upon the nature of both. There may be apparently an entire absence of interaction, as when rosin is shaken up with water or chalk with alcohol. Or, as when sugar is agitated with water, the solid may disappear, entering into solution in the liquid. The study of sugar solution shows quite clearly that the connection of the sugar molecules with each other has been completely destroyed. They are dispersed through the water very much as the molecules of a gas distribute themselves uniformly in a vacant space, and in both cases the permanence of the uniform dispersion is due to the incessant motion of the molecules. Were the molecules at rest, both the sugar and the gas would settle and form a layer on the bottom of the containing vessel.

However, the molecules of the sugar retain their structure intact, the action being limited to their dispersion. When salt, on the other hand, is dissolved in water, a further breakdown occurs, the molecule is separated and ions of sodium and of chlorine move about in the liquid. Both solutions freeze below 0° C. and boil above 100° C. The most important difference between them is that the salt solution conducts the electric current, while the sugar solution is as poor a conductor as water itself.

A fourth possibility presents itself when glue or gelatin is treated with water. The gelatin absorbs water, swells up and, under the influence of heat, dissolves, but the liquid freezes and boils at practically the same temperatures as pure water. The study of the solution shows that the dispersion is not molecular. The particles of gelatin in it are composed of variable

<sup>\*</sup> Presented at the meeting of the Section of Physics and Chemistry held Thursday, April 10, 1913.

and rather large numbers of molecules. A system like this gelatin solution which presents a case of very fine but not molecular subdivision is called a *colloidal solution*. There are certain solids such as gelatin and dextrin (with water), rubber (with benzene and carbon disulphide), which, when they dissolve in liquids, are invariably dispersed in this way. Such solids may properly be referred to as *colloids*. They are all amorphous. Crystallized substances never yield colloidal solutions by mere spontaneous solution in a liquid. They always produce molecular or ionic dispersions. However, the phenomenon of colloidal solution is perfectly general, and crystallized substances can also be obtained in this condition, but not by mere solution.

It is an interesting fact that a substance which yields a colloidal solution with one solvent may form an ordinary molecular solution with another. Soap is an example. Its concentrated solution in water boils at about 100°, freezes at about 0°, and exhibits the behavior of a colloidal solution in general. On the contrary, a soap solution in alcohol shows the normal change in freezing, and boiling points corresponding to the molecular weight, and conducts itself in all respects like an ordinary molecular dispersion.

#### II.

Every one is familiar with the distinctions between solutions and suspensions. Suspensions are turbid in aspect, and the solid can be removed by letting it settle, or by filtration. Solutions are clear, dissolved matter does not subside and is unaffected by filtering. Colloidal solutions occupy an intermediate position.

Consider for a moment the effect of increasing subdivision on a suspension of finely-divided gold in water. So long as the diameter of the particles is much greater than a thousandth of a millimetre, the system will be turbid and the gold will settle rapidly. But the wave-length of visible light ranges between 0.4  $\mu$  and 0.7  $\mu$ , and when the particles become smaller than this they can no longer reflect light and the liquid will appear clear. At the same time there will be a rapid falling off in the speed of settling. Stokes has derived a formula for the velocity of sub-

<sup>&</sup>lt;sup>1</sup> It is usual to employ the symbol  $\mu$  (the Greek letter mu) for the thousandth of a millimetre. In the same way  $\mu$   $\mu$  indicates the millionth of a millimetre.

sidence, v, of small spheres of radius R and density S falling in a liquid of density S' and internal friction f under the force of gravity g:

$$V = \frac{2}{9} g (s - s') \frac{R^2}{f}$$

Substituting the proper values for gold and water and assuming a radius of  $\mu$  for the particles, the value for V is about 14 centimetres per hour. This means, of course, that the system would be a coarse suspension and would clear up at once. But when  $R = 10 \ \mu \ \mu$ , V is only about a centimetre a month. This begins already to be fairly permanent. It must be remembered that the high density of gold (19.5) increases the rapidity of subsidence. If we make the calculation for S = 3, which is about the density of arsenious sulphide, V comes out only about a millimetre a month.

So much for calculation. Now what are the facts? As a matter of fact, the dispersed substance in a colloidal solution does not settle at all, so long as the subdivision is maintained. Colloidal gold solutions have been preserved unchanged for years. I have a solution of arsenious sulphide which has remained apparently unchanged for three years and whose countless particles can readily be seen, engaged in their incessant Brownian movement, with an ordinary oil immersion lens. Whenever settling does occur, it is preceded by the aggregation of the particles into larger particles, which finally attain a diameter of  $\mu$  or over, and slowly subside.

Here, then, is an apparent discrepancy between Stokes's law and the facts. The law informs us that the speed of subsidence decreases rapidly with decreasing radius of the particles, but it does not lead us to expect the total absence of settling which presents itself when the average radius is 10  $\mu$   $\mu$  or thereabouts.

The explanation, of course, is molecular motion, or, in other words, *heat*. The particles are battered, on all sides, by a hailstorm of molecular impacts. If the particle is large, the blows of the molecules of the solvent in different directions neutralize each other. But when the particle is not so very much larger than the molecules themselves a molecule striking, say, on the left, will give the particle a very perceptible push toward the right. "just as a cork follows better than a large ship the motion

Vot. CLXXVI, No. 1053-23

of the waves of the sea." As the dimensions of the particle approach the molecular dimensions it begins to behave like a molecule and is swept along in the endless molecular movement. The cause which prevents the particles in a colloidal solution from settling is in no way different from the cause which prevents the earth's atmosphere from subsiding to a snowy layer a few feet deep on the surface of the planet.

It is worth remembering, also, that the particles of the dispersed phase ordinarily possess an electric charge, which is usually negative. The effect of the repulsion of these similar charges would be to preserve the distribution of the particles throughout the liquid. It is a fact that, when the charges are removed, the system becomes instable and subsidence—preceded by coalescence of the small particles—readily, but not necessarily, occurs.

## III.

On the subject of the classification of colloid systems we must be very brief. One proposal subdivides them into suspensoids. such as the sols of gold and arsenious sulphide, in which the dispersed phase is solid, and emulsoids, in which the dispersed phase is liquid. This classification would appear to be an attempt to extend the familiar distinction between liquid and solid to a domain in which that distinction has little if any meaning. To assert that a thing is solid is to say that it has a definite shape, which it retains with some persistence. There is not the slightest reason to think that the particles in a gold sol are solid. It is usual to assume that they are spherical, but this is done merely because it is the simplest assumption to make. There are faint indications that they really have the form of leaflets or of little rods, but they appear in the ultra-microscope simply as brilliant dancing points, and in reality we know nothing whatever about their shape. In connection with this it is interesting to recall the fact that the formation of a crystal begins with the appearance of minute liquid spheres (globulites)4, which pass

<sup>&</sup>lt;sup>2</sup> Perrin.

<sup>&</sup>lt;sup>3</sup> Thomas Graham introduced the term sol as an abbreviation for colloidal solution.

<sup>&#</sup>x27;Fink, "Poggendorff's Annalen," vol. 46, p. 258 (1839); Schmidt, "Liebig's Annalen der Chemie," vol. 53, p. 171 (1845); Frankenheim, "Poggendorff's Annalen," vol. 111, p. 1 (1860).

through several stages (margarites, longulites, etc.) before the crystal is formed. It seems possible that, under such enormous subdivision, cohesion retires into the background and surface tension assumes the chief rôle, so that the gold particles are rather to be compared to minute drops than to little crystals.

Enough has been said to make clear the uncertainty which attaches to the attempt to classify colloid solutions according to the state of aggregation of the particles. A better classification is into reversible and irreversible colloids, according to the way in which the dissolved substance behaves when separated from the solution. Thus, when a gelatin solution is evaporated until it "sets" it is only necessary to warm the jelly with water to obtain it again in colloid solution. Gelatin is a typical reversible colloid. But when the gold is caused to separate from a gold sol-which can easily be brought about by adding any electrolyte to the sol-the gold will not again enter into colloidal solution. Shaking or warming with water gives a mere suspension, which settles at once. Gold is an irreversible colloid. The distinction is fundamental. Many organic colloids are reversible, while it is rather the habit of the inorganic colloids to behave in the irreversible way.

### IV.

In order to prepare a sol containing an irreversible colloid all that is necessary is to reduce the solid to extreme subdivision in a liquid in which it is insoluble. The electric arc furnishes a rapid and simple method.<sup>5</sup> Two gold wires about 2 mm. thick are connected with a 220-volt circuit and brought together under distilled water. A 110-volt circuit can be used, but more patience is required. Sols of platinum, silver, copper, and other metals can be made in the same way. By related electrical methods, using such liquids as pentane and anhydrous ether, Svedberg<sup>6</sup> obtained sols of all five of the alkali metals. The colors of the sols agreed with those of the vapors of the corresponding metals.

<sup>&</sup>lt;sup>5</sup> Bredig, Zeitschrift für angewandte Chemie, 1898, p. 951. For a full account of Bredig's work with the platinum sol see Zeitschrift für physikalische Chemie, vol. 31, pp. 258–353 (1899).

<sup>&</sup>lt;sup>6</sup> Berichte der deutschen chemischen Gesellschaft, vol. 38, p. 3616 (1905).

Chemical reduction of a salt of a metal furnishes another method which has been largely employed by Zsigmondy and other investigators. For instance, a very dilute solution of auric chloride is mixed with such reducing agents as formaldehyde, hydroxylamine or an ethereal solution of phosphorus. The gold sols obtained in this way are usually red by transmitted light, the particles being bright green and very much smaller than in the sols obtained by the electrical method.

By various chemical methods, which lack of space forbids us to discuss, sols of sulphides (CdS,  $As_2S_3$ ,  $Sb_2S_3$ , etc.) and oxides (Fe<sub>2</sub>O<sub>3</sub>,  $Al_2$ O<sub>3</sub>) can be obtained. The sol of aluminum oxide is important on account of its connection with dyeing and mordanting. The formation of the blood-red sol of ferric oxide by adding a concentrated solution of ferric chloride to about 50 volumes of boiling distilled water is a simple and beautiful lecture experiment.

In making colloidal solutions of salts, the essential thing is to mix dilute solutions of the precipitants, using a liquid in which the insolubility of the product is as complete as possible. Thus, in mixing very dilute solutions of sodium sulphate and barium chloride, a crystalline precipitate is usually obtained. The reason is that barium sulphate possesses a very slight but real solubility in water. Hence the liquid in contact with the particles first formed contains enough barium sulphate to nourish their growth and allow them to develop to crystals. If alcohol is added to the sulphate, before the barium chloride is introduced, the solubility of the barium sulphate is greatly reduced, and it is obtained in colloidal solution without difficulty.

In the same way if we mix water solutions of sodium hydroxide and of hydrochloric acid we obtain merely an ordinary solution of common salt. But if salt is produced by a reaction between organic compounds in a liquid in which the sodium chloride is insoluble, then a colloidal solution is obtained. For instance, when chlor-acetic ester interacts with sodio-malonic ester a grayish opalescent sol of sodium chloride in ethenyl tri-carboxylic ester results:  $CH_2Cl\ COOC_2H_5$  +  $CHNa\ (COOC_2H_5)_2 = CH_2\ (COOC_2H_5) - CH\ (COOC_2H_5)_2 + NaCl.$ 

<sup>&</sup>lt;sup>7</sup> See his monograph, "Zur Erkentniss der Kolloide" (Jena, 1905), which has been translated by Jerome Alexander.

At low temperatures, in such liquids as toluene and chloroform, even *ice* has been obtained in colloidal solution.

#### V.

The most striking property of the reversible colloids is that they are able to communicate their reversibility to the irreversible ones. Thus, if a trace of gelatin is added to a gold solution, the gold becomes much more difficult to coagulate by electrolytes, and when coagulated it can be dispersed again by merely warming with water. This curious protective action is exerted, in greatly varying degree, by most reversible colloids. Direct study of the phenomenon with the ultra-microscope shows that the view frequently expressed that the gelatin envelops or forms a film around the gold particles is incorrect. What actually happens seems to be a direct combination between gelatin particles and gold particles, which then pass through the reversible changes together.

Protective colloids enjoy a wide practical application. In the manufacture of photographic films the gelatin retards the crystallization of the silver bromide. Ink often contains a colloid which prevents the pigment from settling. The lubricant "aqua dag" put in the market by the Acheson Company consists of finely-divided artificial graphite, held up by a protective colloid. Clay is made plastic for the potter by an empirical process which involves the action of protective colloids derived from decaying vegetable matter. The addition of gelatin in making ice cream depends upon its protective action in preventing the growth of ice crystals, which would make the product "gritty." Without doubt protective action plays an important rôle in the cleansing action of soap. This has been made clear by some recent experiments of Spring.8 Lampblack, freed from oil by long washing with alcohol, ether, and benzene, forms a rather stable suspension in water, but the lampblack is detained by a paper filter. If the filter is now reversed, so that the blackened surface is outward, and water poured through it, the lampblack is not removed, but a dilute soap solution removes the coating and cleanses the filter at once. Finally, lampblack suspended—or colloidally

<sup>&</sup>lt;sup>8</sup> Kolloid Zeitschrift, vol. 4, p. 161 (1909); Kolloid Zeitschrift, vol. 6, pp. 11, 109, 164 (1910).

dissolved—in soap solution, passes through a filter unchanged. It is of much practical interest that there is a well-marked optimum in the concentration of the soap required to protect the lampblack. A one per cent. soap solution is the most efficient. In two per cent. soap solution lampblack sinks about as rapidly as in pure water.

## VI.

We have already considered the probable actual condition of the particles in a colloidal solution and have concluded that, for the present, no very definite information is obtainable about the matter. We must now return, for a moment, to the subject in order to allude to the thesis so brilliantly advocated by van Weimarn, the Russian investigator, who holds that the particles are of necessity minute crystals and that there is, in fact, no such thing as amorphous matter. He even goes so far as to state that substances like air and water are in a "dynamic crypto-crystalline condition," though I have been unable to understand what he means by this statement.

Briefly, the evidence that van Weimarn adduces to the support of his hypothesis is:

(1) That colloid particles will grow to crystals if provided with the proper nourishment, namely, a dilute solution of the same substance.

(2) That colloid particles are capable, when introduced into a supersaturated solution of the same substance, of discharging the supersaturation and inducing the formation of crystals.

Those who desire to follow this matter further should read van Weimarn's little book, "Grundzüge der Dispersoidchemie," after which they will find themselves very much interested, but somewhat unconvinced. Let me hasten to add that I have not the least desire to undervalue the brilliant experimental work of the Russian chemist. It is, in fact, precisely by the conception of more or less daring hypotheses, and the working out of their consequences, that our science achieves its endless victory over the nescience about us.

## VII.

We have seen that the wave-lengths of the visible radiations are comprised between 0.4  $\mu$  and 0.7  $\mu$ . With objects much

smaller, the ordinary microsopic method ceases to be applicable. Using ultra-violet radiation for illumination, quartz lenses in the microscope, and receiving the image with the photographic plate instead of the eye, it is possible to advance a step further in the domain of the infinitesimal, but only a step, and there are obvious objections to the proceeding. Since some of the particles in colloidal solutions are only  $0.006 \mu$  in diameter, we can never hope to see them as little bodies subtending a visual angle. The ultra-microscope—the powerful instrument of investigation to which most of our knowledge of colloid systems is due-renounces this idea and makes the particles visible merely as glittering points on a black background. The sol is placed in a small rectangular glass trough and a horizontal beam of arc light or sunlight focussed in it. The microscope is placed vertically above the trough. It will at once be seen that there are two fundamental things about the instrument: to provide intense illumination, and to make sure that no light enters the microscope except the rays which emanate from the particles. The principle is simple, but the system of diaphragms and lenses needed to secure the second object makes the ultra-microscope an elaborate and expensive instrument in practice.

Cotton and Mouton<sup>9</sup> achieve the same end in a different way. The illumination (arc or sunlight) is thrown up from below by a paraboloid reflector so ground that all rays, except those diffracted by the particles, are totally reflected from the coverglass over the sol. This instrument is simple, easily adjusted and cheap. It is made commercially by the firm of Zeiss. It would seem to be admirably adapted to school purposes. In fact, after a look into the ultra-microscope, the study of the molecular topics ceases to be drudgery and becomes a positive intellectual

need.

#### VIII.

Even a brief glance at the subject of colloid systems must at least mention the classic work of Perrin<sup>10</sup> on the distribution of

<sup>o</sup> Compt. Rendus, vol. 136, p. 1657 (1903).

<sup>&</sup>lt;sup>10</sup> Annales de Chimie et de Physique, 3d series, vol. 18, p. 5 (1909). There is a German translation by Donau in Kolloidchemische Beihefte, vol. I, p. I (1910). An English translation by Soddy has appeared in book form under the title "The Brownian Movement and Molecular Reality."

the particles in suspensions of gamboge and mastic. He succeeded, by an ingenious and simple method, in preparing emulsions of gamboge in water in which the spherical yellow granules were all of the same diameter. If we consider a mass of such a liquid in a tube, it is clear that the granules, if at rest, would, since they are denser than water, all fall to the bottom. fact that they remain suspended is due to their movement. other words, the state of things is the same as in the earth's atmosphere, and just as the molecules are more crowded near the earth's surface, so the granules of gamboge must be more numerous near the bottom of the liquid than in the upper layers. Perrin verified this prediction by direct counting of the granules under the microscope. The barometric formula which describes the progressive rarefaction of air with increasing height also describes the distribution of the granules in Perrin's uniform emulsions. The only difference is that, while the aviator must ascend six kilometres in order to reach air half as dense as at sea level, the same effect is produced, in Perrin's emulsion, by an ascent of o.t millimetre

That the mean energy of rotation of a molecule must be equal to its mean energy of translation is one of the chief propositions of the kinetic theory. Perrin has proved this by direct measurement of the rotation of granules under the microscope. this purpose, large granules (15  $\mu$ ) of mastic were employed. These are far too heavy to remain suspended in water, so a solution of urea was used. Fortunately, the granules contain little inclusions which make it possible to measure their rotation.

These are only two of many fundamental results contained in this wonderful memoir. Van't Hoff extended the gas laws to solutions. Perrin has now proved them to be valid for systems in which the moving particles are visible realities. Let us end by quoting one of the sentences of his conclusion:

"La découverte de telles relations marque le point où s'élève. dans notre conscience scientifique, la réalité moléculaire sous-

iacente."

#### NOTES FROM THE U.S. BUREAU OF STANDARDS.\*

#### THE METRIC CARAT.†

Beginning July 1, 1913, the Bureau of Standards will recognize the metric carat of 200 milligrammes as the unit of weight for diamonds and other precious stones, and will use this unit for purposes of certification of all carat weights submitted to the Bureau for test. On the same date the Treasury Department of the United States Government will also begin the use of this unit in the customs service for the levying of import duties on precious stones. This unit will also be put into commercial use in the United States on this date by practically all the dealers in gems and precious stones through the efforts of a committee representing all the principal firms handling gems.

The Bureau has therefore taken this opportunity to issue a circular giving tables of the relations between the carat weight in former use in this country and the new metric carat, together with other information that may be of interest at this time in connection with the subject.

The carat weight in use in different countries has, in the past, differed greatly, scarcely any two countries of importance having the same standard. Even within the United States there has not been agreement in the standard used, the various makers of weights using slightly different quantities as a standard. This has led to a great deal of confusion in the weighing of gems, which has been the more serious because of the great value of the article.

Recently, however, the movement for the adoption of a uniform standard has met with increasing success, and the metric carat of 200 milligrammes has been adopted by Spain, Italy, Bulgaria, Denmark, Norway, Japan, Portugal, Roumania, Switzerland, Sweden, France, Germany, and Holland, while considerable progress has been made toward its adoption in England and Belgium.

<sup>\*</sup> Communicated by the Bureau.

<sup>†</sup> Circular of the Bureau of Standards, No. 43.

The carat which has been in use heretofore in the United States, while varying, has been nearer the value 205.3 milligrammes than any other. This value has therefore been taken in making up the tables of equivalents given in this circular. This old carat has usually been subdivided on the binary system, the smallest subdivision used being, usually, one sixty-fourth of the carat. One of the improvements introduced with the new system is the subdivision of it on the decimal system. Tables are given both for the conversion of fractions of an old carat to decimals of the metric carat and for each whole carat from I to Ioo in terms of the new, and vice versa.

Suggestions are also given for the improvement of weighings of precious stones, including the necessary features of a good balance, its use and care, the characteristics of the best kind of weights for the purpose, the method of their adjustment and the tolerances that will be allowed under the Bureau's Class C tests of such weights, the protection and handling of the weights and their certification. It is recommended that a small letter "c" without a period be used as an abbreviation for the metric carat in conformity with the system of abbreviations used in the metric system, the abbreviation "car." having been used heretofore for the old carat.

# METHODS OF ANALYSIS OF STANDARD ANALYZED SAMPLES.\*

A NEW edition of Circular No. 14 gives the revised methods of analyses employed in the preparation of the series of standard analyzed samples issued by the Bureau of Standards for checking the accuracy of commercial analyses. Some of the Bureau's methods have undergone modification from time to time and as given apply mainly to the irons and steels recently issued.

The earlier samples were analyzed usually only by the rapid technical methods used more or less generally by the steel trade. The analyses made by the other coöperating chemists were mostly of the same type. The object on the one hand was to indicate the order of agreement which might be expected from careful analysis, using these methods and working on a homo-

<sup>\*</sup> Bureau of Standards Circular No. 14, 4th edition.

geneous material, and on the other hand to supply samples of which the composition was known within the limits of error indicated by the results published on the certificates. It is therefore emphasized here that the Bureau's analyzed irons and steels are "standardized" only in this sense. In other words, the figures on the certificates are perhaps to be regarded as a criterion of the existing state of the analytical chemistry of this class of materials, and of methods, and they no doubt represent fairly well the result which may be expected by attempting to fix the composition of such materials in this way. It should be remembered, however, that the composition so determined is not necessarily the absolute or correct one, and that judgment should be used in the application of the data afforded by the certificates. An illustration will make this clear.

Scrutiny of all the earlier iron and steel certificates issued shows that the color method for manganese has furnished results over 5 per cent. higher on the average than were obtained by the other methods combined. Without raising the question whether the average of the color results or that of the others is nearer the truth, it is clear that both cannot be correct, and that their "general average" must probably be in error. Hence, an analyst, using the samples, is justified in respecting the "general average" if experience has convinced him that the average for any particular one of the methods tabulated is worthy of greater credence. Further, for instance, it would be manifestly wrong to use any one of the general averages for manganese (possibly in error by one or more per cent. of the manganese) for the standardization of a volumetric solution that is to be used for a ferromanganese alloy or a manganese ore.

No doubt the above cautions will be found applicable to some of the other common elements as well as to manganese, but, owing to the much smaller percentages of most of those others, their errors are not as a rule so immediately apparent nor so amenable to the corrective study which the Bureau hopes to take up in time.

Closer approximation to the truth might be obtained through determinations by a greater variety of technical methods, or with better promise of success by the longer and perhaps more exact methods not generally used for technical work, or by correcting for some more or less obvious sources of error often overlooked by the technical analyst. The amount of work to be thus expended on a given sample must be regulated by the importance of higher accuracy to those who use the sample. The Bureau endeavors to have the results by its own chemists well within the limits of error permissible in practical work. These in turn are governed by such factors as the degree of segregation in ingots, castings, etc., the difficulties of sampling large lots of material, etc. At present it is believed that in the steel and iron industry most of the technical analytical methods are capable of yielding results quite up to, if not in advance of, the requirements of practice.

## THE TESTING OF MATERIALS.\*

Many inquiries are received by the Bureau of Standards regarding the testing of materials. A new circular now in press is designed to furnish information upon some of the more general aspects of this branch of the Bureau's work. The circular is intended mainly for the user or buyer of materials rather than the industrial expert. The aim is to outline briefly with respect to each class of material the tests usually made, the conditions under which such work is undertaken, and some of the limitations due to the status of technical knowledge. Such testing is mainly for the Government Departments or where an authoritative test is required.

The testing of materials serves two important and distinct purposes: First, to ascertain whether or not they comply with specifications; and, second, to add to the general fund of knowledge regarding them. When done with both objects in view it ceases to be of merely transient value for the immediate case in hand, important as this may be, but adds to the world's useful knowledge of the materials. Data accumulate rapidly in the regular work of the testing laboratory, and when properly correlated they yield information of permanent value in the industries.

The utility of materials depends upon the nature, magnitude, and stability of their properties. To determine these is the object of the testing of materials. For a complete study of the properties of a material all of its properties would have to be

<sup>\*</sup> Bureau of Standards Circular No. 45.

studied through all ranges of conditions. Considerations of economy generally make such full tests impracticable, although the conviction is growing that the systematic study of the properties of materials would be a most effective means of technical progress.

The degree of accuracy to be sought becomes a very practical matter in a testing laboratory. The time and labor involved in such tests increase out of proportion as the limits of attainable accuracy are approached. For the determination of physical constants or fundamental properties of materials the degree of accuracy sought may be the maximum possible. For example, a minute may suffice to determine the density of alcohol for commercial purposes by means of a hydrometer. Months, however, may be well spent in a precise determination of its density as a physical constant of great technical importance. In general the degree of accuracy striven for should be that which is strictly good enough for the purpose in hand—whether the work be routine testing or scientific research. The selection of the degree of accuracy to be sought for in each case requires the experience and judgment of the specialist.

The time has passed when the strength of materials can be left to guesswork or even to intelligent opinion alone. With the rapid increase in the height of buildings, length of span for bridges, and speed of transportation, new problems in safety and efficiency arise. The testing laboratory can test these materials by sample in advance of their use, and by means of the strain gauge can determine the net strain of the structure during its construction and after erection or assembling. Suitable tests during and after construction might be prescribed in building or inspection regulations and made part of the original specification in all cases. Under these circumstances the responsibility for failure of structures must rest with those who knowingly omit adequate tests where such are available.

The circular treats of the more usual tests applied to the various materials. In many cases the best methods for testing have yet to be devised. As rapidly as practicable, the Bureau is selecting or developing standard methods of testing each useful quality of materials. This leads directly to the establishment of specifications or standards of quality.

Ideal standards of quality in most cases are still imprac-

ticable through lack of data, and the practical step has been the tentative specification. The specification is designed to obtain the quality best suited to the case in hand, and usually reflects the status of knowledge upon this subject. To the extent that it embodies the results of experience, it is the best that can be done until rigorous standards of quality are developed. Inflexible specifications retard technical progress; but if allowed to advance apace with new technical knowledge, the specification becomes a distinct aid to such progress.

With the large variety of tests which may be made of a given material those should be selected which suffice to show with commercial accuracy its fitness for the purpose in view. Economy dictates this limitation, since in many cases the time and labor needed for more elaborate tests would make them prohibitive, and nullify the economic value of such testing. Tests of quality may be made with varying degrees of completeness except where existing specifications define the tests to be applied. Even such tests may be modified in emergencies.

A brief outline of tests applicable to the several classes of material will be found in this circular. The treatment, in the nature of the case, is usually incomplete. Where definite tests cannot yet be announced, the Bureau will endeavor to furnish information and possibly arrange special tests. In making these tests and investigations of materials for the Government, and in special cases for others, the Bureau secures much valuable information as to the nature and use of the materials and the specifications and methods of testing. This is always available to manufacturers, private testing laboratories, and the public. While the results of any single test may be for a particular object, the general information which accumulates at the Bureau is of wider interest and application.

Among the sections of the circular may be mentioned Metals, Cement, Ceramics, Lime, Stone, Paints and Paint Materials, Bituminous Material, Inks, Paper, Textiles, Rubber, Leather, Lubricating Oils and Greases, Chemicals, and Miscellaneous and Technical Materials.

Copies of the circular may be obtained by those interested upon request.

## HIGH-FREQUENCY AMMETERS.

By J. H. Dellinger.

The following is an abstract of an extended paper dealing with the measurement of high-frequency currents, to be published in the Bulletin \* of the Bureau of Standards.

For the measurement of current at radiotelegraphic frequencies, 50,000 to 2,000,000 cycles per second, it is general practice to use the hot-wire ammeter or a modification of it. Its superiority is due to the simplicity of form which the portion of the circuit within the instrument may have, permitting a minimum of self-inductance and capacity. When the instrument is required to carry relatively large currents, a simple single wire is not sufficient, and more than one elementary path must be provided for the current. Then the current distribution, and consequently the indicated current, changes as the frequency is varied, because at low frequencies the current distribution is determined solely by the resistance, while at high frequencies the inductances predominate. There are three general types of ammeters for large currents of high frequency: (a) that employing wires in parallel, (b) the so-called unshunted ammeter in which a single wire has different portions of its length in parallel, and (c) the ammeter employing thin metal strips. All types in use are found to be subject to serious errors at radiotelegraphic frequencies.

In the case of the parallel wire ammeter, mutual inductances between parts, which had hitherto been supposed negligible, are the determining factor in the change of current distribution. It is an interesting fact that these changes come just in the range of radiotelegraphic frequencies. In the so-called unshunted ammeter the errors are chiefly due to the self-inductances of parts other than the hot wire. They can be minimized by symmetrical location of the current leads. In the strip ammeter the terminal blocks have been found to be the source of large errors. These are reduced by proper shaping of the blocks.

One effective means of reducing the errors of these ammeters at high frequencies is by using working parts of high resistance,—i.c., metal which is both very thin and of high resistivity.

<sup>\*</sup> Bureau of Standards Scientific Paper No. 206.

Another expediency which was found successful was to change the design so that the deflections depended on the entire heat production in the instrument instead of on that in one branch of its circuit. Still another method of improvement is to arrange the working parts (either wires or strips) as equidistant elements of a cylinder, so that each has the same set of mutual inductances. Even this design, in common with the others, is subject to an error which has hitherto been overlooked. It is very difficult to obtain very thin wires or strips of uniform cross-section, and this variation results in the resistances of elements being unequal while the inductances are substantially equal.

The induction of eddy currents in neighboring masses of metal is found to cause no error. Inductive action of the leads near an instrument in some cases appreciably affects the readings. The distributed capacity of the circuits within the instruments is found to cause no error, but the capacity of auxiliary parts produces an appreciable effect at the highest frequency used, 1,500,000 cycles per second. This effect was very striking, two instruments in series carrying different amounts of current. A way was found to eliminate the effect, for the purposes of ammeter comparison.

The experiments on the various types of instrument were corroborated by theoretical calculation. The formulas for self and mutual inductances of short parts of a circuit were shown to hold for this kind of work. From the standpoint of pure science, this is one of the most interesting results of the investigation.

The Influence of Hot Caustic Lye on the Strength of Cotton Goods. R. Bude. (Färber. Zeit., xxiv, 159.)—Gray cotton cloth was treated with caustic lye of 8°, 12°, and 18° Bé., containing 5.29, 8.00, and 12.64 per cent. NaOH respectively, no tension being applied. After washing thoroughly, the cloth was boiled under pressure and bleached. Strength determinations were made on warp and weft threads. Duplicate tests were made on heavier cloth, and also with the same cloth after dyeing and finishing. In all cases the strength was increased. Also the loss in weight decreased as the concentration of the caustic soda increased. The increased strength is probably due to the formation of a cellulose hydrate, the factors which influence the change probably operating through their effect on the osmotic pressure of the solution.

## THE FRANKLIN INSTITUTE

#### LIBRARY NOTES.

#### Purchases.

CLAUDE, G.-Liquid Air Oxygen, Nitrogen. 1913.

Hænig, A.—Emery and the Emery Industry. 1912.

HUYGENS, C.—Die Pendeluhr horologium Oscillatorium. 1913.

International Catalogue of Scientific Literature: A.—Mathematics, 11th issue. 1913. F.—Meteorology, 10th issue. 1913.

KEILHACK, K.-Lehrbuch der Grundwasser- und Quellenkunde. 1912.

Loschmidt, J.—Konstitutions-formeln der organischen Chemie. 1913.

PLOTNIKOW, J.—Photochemische Versuchstechnik. 1912.

RIMMER, E. J.—Boiler Explosions, Collapses, and Mishaps. 1912.

Suevern, C.—Die künstliche Seide. 1912.

SCHMEITZNER, R.—Grundzüge der mechanischen Abwässerklarung. 1908. THORPE, E.—Dictionary of Applied Chemistry, vol. 4.

#### Gifts.

American Mining Congress, Report of Proceedings, vol. 15, 1912. Denver, 1912. (From the Congress.)

Baker Ice Machine Company, Catalog Nos. 30 and 31. Omaha, no date. (From the Company.)

British Association for the Advancement of Science, Report of the 82d meeting, 1912. London, 1913. (From the Association.)

Buffalo Forge Company, Catalog Nos. 225 and 256. Buffalo, no date. (From the Company.)

Canada Department of Trade and Commerce, Report for 1912, part 5: Grain Statistics. Ottawa, 1913. (From the Department.)

Canadian Society of Civil Engineers, Report of Annual Meeting, vol. 27, 1913. List of Members, 1913. Montreal, 1913. (From the Society.)

Chicago School of Civics and Philanthropy, Announcements 1913–1914.

... Chicago, 1913. (From the School.)

Foster Engineering Company, Catalogue 20 F. Newark, 1913. (From the Company.)

Garlock Packing Company, Catalogue O, 1913. Philadelphia, 1913. (From the Company.)

Harrison Safety Boiler Works, Catalogue No. 500: Cochrane Heaters. Philadelphia, 1911. (From the Works.)

Illinois State Geological Survey, Bulletin No. 25: Report and Plans for Reclamation of Lands Subject to Overflow in the Embarrass River Valley, by Jacob A. Harman. Urbana, 1913. (From the Survey.)

Vol. CLXXVI, No. 1053-24

Iowa State College, General Catalogue 1913-1914. Ames, 1913. (From the College.)

Iron and Steel Institute, Carnegie Scholarships, Memoirs, vol. 5, 1913. London, 1913. (From the Institute.)

Jones Cold Store Door Company, Catalogue No. 5. Hagerstown, 1913. (From the Company.)

Kaiserlich Leop.-Carol. Deutsche Akademie der Naturforscher: Nova Acta, Band 96 and 97; Leopoldina, Heft 48. Halle, 1912. (From the Akademie.)

McGill University, Calendar 1913-1914. Montreal, 1913. (From the University.)

Manchester Board of Water Commissioners, 41st Annual Report, 1912. Manchester, 1913. (From the Board.)

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation Bulletin No. 2, Bibliography of Smoke and Smoke Prevention. Pittsburgh, 1913. (From the Institute.)

Mysore Meteorological Department, Report on Rain-fall Registration, 1911. Bangalore, 1913. (From the Department.)

National Fire Protection Association, Proceedings of the 17th Annual Meeting, 1913. Boston, 1913. (From the Association.)

National Park Conference, Proceedings held at Yosemite National Park, October 14-16, 1912. Washington, D. C., 1913. (From the U. S. Government.)

New South Wales Department of Mines, Annual Report 1912. Sydney, 1913. (From the Department.)

New York Public Service Commission for First District, New Subways for New York: The Dual System of Rapid Transit, June, 1913. New York City, 1913. (From the Commission.)

Ontario Bureau of Industries, Annual Report 1911. Toronto, 1912. (From the Department of Agriculture.)

Ontario Department of Agriculture: Report of the Minister of Agriculture, 1912; Report of the Farmers' Institutes, 1911 and 1912; 38th Annual Report of the Ontario Agricultural College and Experimental Farm, 1912. Toronto, 1913. (From the Department.)

Queensland Under Secretary for Mines, Annual Report, 1912. Brisbane, 1913. (From the Mines Department.)

Report on the Progress of Agriculture in India for 1911-1912. Calcutta, 1913. (From Inspector-General of Agriculture.)

The Story of Nineteenth-Century Science, by Henry Smith Williams, and Principles of Animal Mechanics, by Rev. Samuel Haughton. London, 1901 and 1873. (From Mr. George W. Shellem.)

University of Louisville, Catalogue 1913-14. Louisville, Ky., 1913. (From the University.)

University of Montana, Register 1910-11, 1911-12, 1913-14. Missoula, 1911-1913. (From the University.)

University of South Carolina, Catalogue 1912-1913. Columbia, 1913. (From the University.)

University of Texas, Catalogue 1912-1913. Austin, 1913. (From the University.)

Waltham City Documents, 1912. Waltham, Mass., 1913. (From the City Clerk.)

Washington State College, Catalogue 1913. Pullman, 1913. (From the College.)

Western Australia Geological Survey, Bulletin No. 42; Contributions to the Study of the Geology and Ore Deposits of Kalgoorlie, East Coolgardie Goldfield, part 1, by E. S. Simpson and C. G. Gibson. Perth, 1912. (From the Agent-General for Western Australia.)

#### PUBLICATIONS RECEIVED.

Electric Arcs: Experiments upon Arcs between Different Electrodes in Various Environments, and their Explanation, by Clement D. Child, Ph.D., Professor of Physics at Colgate University. 194 pages, illustrations, 12mo. New York, D. Van Nostrand Co., 1913. Price, \$2.

An Elementary Treatise on Calculus: A Text-book for Colleges and Technical Schools, by William S. Franklin, Barry MacNutt, and Rollin L. Charles, of Lehigh University. 253 + 41 pages, illustrations, 8vo. South Bethlehem, Pa., authors, 1913.

Iowa State College of Agriculture, Engineering Experiment Station, Bulletin No. 32: A Topographical Survey of the Spirit and Okoboji Lakes Region, by H. C. Ford. 38 pages, illustrations, maps, 8vo. Ames, Iowa, College, 1913.

Les Propriétés optiques des Solutions par C. Chéneveau, Docteur ès Sciences. 240 pages, illustrations, 8vo. Paris, Gauthier-Villars, 1913. Price, in paper, 10 francs.

Cyanamid Manufacture, Chemistry and Uses, by Edward J. Pranke, B.Sc. 112 pages, illustrations, 8vo. Easton, Pa., Chemical Publishing Company, 1913. Price, \$1.25.

Treatise on General and Industrial Organic Chemistry, by Dr. Ettore Molinari, Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures and of Merceology at the Luigi Bocconi Commercial University, Milan. Translated from the second enlarged and revised Italian edition by Thomas H. Pope, B.Sc., A.C.G.I., F.I.C. 770 pages. illustrations, 8vo. Philadelphia, P. Blakiston's Son & Company, 1913. Price, in cloth, \$6.

# **CURRENT TOPICS**

On the Troubles which Certain Lightning Conductors, Called "Niagaras," May Cause to Neighboring Postal and Telegraphic Apparatus. J. VIOLLE. (Comptes Rendus, clvi, 520.)—The Postal Administration of France has hitherto followed the course indicated by Melsens for applying the principles of the Faraday cage to lightning conductors protecting buildings. Modern wireless researches have demonstrated the vital importance of the earth connection for currents of very high frequency, and it is now recognized that many lightning conductors are inefficient from indifferent earths, though almost perfect according to old ideas. Further, the ohmic resistance of such a conductor is secondary, its surface, and freedom from bends, being of the greatest importance. An electric "niagara" consists of a long strip of electrolytic copper terminating above and below in clusters of copper points, those at the bottom dipping into a sheet of water. During storms, atmospheric electricity is continuously discharged through the points, whence the name "niagara." No aërial telephone wire should be within 20 metres of such niagaras, or disturbances may result.

Disintegration of Metals at High Temperatures. J. H. T. ROBERTS. (Phil. Mag., xxv, 270.)—The theory has been advanced that the disintegration of the platinum metals was due to direct oxidation. Since platinum does not, under any conditions, combine directly with oxygen, it is generally assumed that the influence of oxygen can only be catalytic, and, moreover, there are certain experimental facts which apparently tend to disprove the theory that the disintegration is due to direct oxidation. In these experiments, in which Wilson's condensation method is adopted, the wire is not placed in the expansion chamber, but in a separate chamber, so that no water drops can fall upon it. The wire is heated by a current developed from an alternator and transformer set. On their way to the expansion chamber the nuclei pass through an annular space, 2 mm. wide, between two brass tubes insulated from one another, the outer one earthed, the inner at -230 volts. There are two well-marked conditions governing the production of nuclei: (1) The recent history of the wire previous to the experi-(2) The length of time since the commencement of experi-There are two sets of nuclei: the first, got rid of after continuous experimenting, depend on the presence of hydrogen and other gases in the wire; the second depends on the presence of oxygen surrounding the wire: the second set are never obtained

below a certain temperature. The metals experimented upon were platinum, palladium, rhodium, ruthenium, and iridium. Platinum begins to disintegrate at as low a temperature as 500° C., but no loss of weight could be detected even after days of heating. The disintegration comes within the range of the balance between 1000° C. and 1100° C. The second set of nuclei, even at 500° C., are very persistent, and do not change in size or character, being produced in pure oxygen, no matter how long the heating has been continued; they are not produced in the absence of oxygen. This shows that they probably are not either particles of the metal brought off by the escaping gas or traces of compounds of different gases. The rate of the loss of weight of the platinum wire is roughly proportional to the oxygen pressure, which points to the formation of an endothermic oxide. Experiments in a constant-volume gas chamber, in which the loss of platinum to the loss of oxygen is determined, give results which in the case of air approximate 2 Pt: O. and in the case of oxygen Pt: 20. It does not seem probable that this large amount of oxygen is simply adsorbed; it must be combined chemically, or, at any rate, for the greater part. During the cooling of the oxide after its formation at the hot wire some decomposition takes place, and the amount of the decomposition will be greater the lower the oxygen pressure. If we assume that the oxygen adsorbed by the deposit is small, the composition of the oxide in the experiments with oxygen must be either PtO, or some higher oxide. If the oxide is also present in the deposit in air, there must be a considerable amount of metallic platinum mixed with it, being the result of dissociation of the oxide during cooling. The formation of an endothermic volatile and dissociable oxide not only explains all the observed facts, but will also explain certain facts in the discharge of negative and positive electricity from hot platinum wires at low pressures.

Change of Volume of Ceramic Raw Materials in Burning. R. RIEKE and K. ENDELL. (Silikat-Zeits., i. 48, 67, 85.)—There are three causes for volume alteration: (1) Transformation from a crystalline to the amorphous state; (2) decomposition into new compounds, and (3) transformation into another crystalline system. Feldspar belongs to the first of these types, kaolin to the second, and quartz to the third. The behavior of various forms of silica during heating is described and the results are applied to practical ceramics. Different sources of raw material, such as the interchange of flint and quartz, undoubtedly affect the behavior of the body, quite apart from their degree of subdivision, and the case may be further complicated by transformation from one form of silica to another during burning. The action of glaze on body is greater when the body is compounded with flint than when compounded with quartz or cristobalite. There are numerous references to previous investigations.

Resistance of Thick Cylinders to Rupture. MALAVAL. (Rev. de Métallurgie, x, 214.)—In a tube of the proportions of gun practice, the thickness about equal to the calibre, there are two distinct periods besides the elastic range. This is followed by the range of semi-elasticity or partial failure, which is of sensibly the same duration in stress. With increasing applied pressures the area of overstressed metal widens radially outwards. Thus if the pressure is released the outer elastic zone is prevented from returning completely to its original shape by the permanent deformation of the inner plastic zone. The mutual action causes the unloaded tube to be stressed in tension in the outer region and in compression in the inner, so that it is in the condition of an ideal shrunk composite tube—i.e., one with an infinite number of indefinitely thin components whose mutual pressures are such that under rising internal pressure all parts reach the elastic limit simultaneously and bear equal parts of the load. The semi-elastic period ceases when the outside layer reaches the limit of elastic deformation and is followed by the periods of general failure. During this period, covering an increase of resistance much greater than those of the first two periods, all parts show an increase of resistance, the inner region being in compression and the outer in tension. It follows that the metal, whose capacity for deformation is greater in compression than in tension, can withstand very considerable internal strains. It is concluded that the ordinary shrinking process might be replaced advantageously by one involving initial overstraining of a solid tube. A gun so constructed would withstand a pressure of over 1500 kilogrammes per square centimetre (213,300 pounds per square inch).

Graphite Industry of Madagascar. Anon. (Board of Trade Journ., June 12, 1913.)—His Majesty's Consul at Antananarivo reports, on the authority of the Chief of the Mining Department of Madagascar, that the graphite industry in the island is making considerable progress, the quantity exported during the first quarter of the year amounting to 980 kilogrammes, as compared with 474 kilogrammes during the corresponding period of last year, and 259 kilogrammes for the corresponding period of 1911. It is believed that by 1916 there will be 20 metric tons exported annually.

Motor Car Bronzes. Anon. (Metal Ind., ii, 7, 298.)—The American Society of Automobile Engineers has adopted the following specification for bronzes: Hard Bronze—Copper, 87–88 per cent.; tin, 0.5 to 10.5 per cent.; and zinc, 1.5 to 2.5 per cent. Gear Bronze—Copper, 88–89 per cent.; tin, 11 to 12 per cent., and phosphorus, 0.15 to 0.30 per cent. The hard bronze is similar to the United States Government bronze G, and has a tensile strength of approximately 35,000 pounds per square inch. The gear bronze is commonly known as English gear bronze.

Argon and its Production. SIR W. RAMSAY. (Chem. Trade Jour., lii, 595.)—After referring to earlier work on the action of niton (radium emanation) on various substances, and the formation of helium and neon by the bombardment of the glass of a vacuum tube by cathode rays in the presence of hydrogen, the writer states that he has confirmed the results of Collie and Patterson, and believed that under the experimental conditions dry hydrogen polymerized into helium, while oxygen was necessary for producing neon, which might be derived from moisture or from the bombarded glass. On allowing the electric discharge to pass for five or six hours between the aluminum cathode and an anode of aluminum coated with sulphur in a vacuum tube into which dry hydrogen was introduced, evidence was obtained of the formation of argon, but no trace of neon or helium could be detected. In an analogous experiment, using selenium instead of sulphur, the gas obtained, when examined spectroscopically, showed very faintly the characteristic yellow and green lines of krypton.

Annealing of Hardened Products. L. GUILLET. (Rev. Mét., x, 665.)—The tensile strength, elastic limit, and elongation of hardened nickel and steel were determined in the original condition, and after annealing in a salt bath at temperatures from 100° C. to 900° C., and the results are tabulated and graphically illustrated. It is shown that the first deflection from the original as the result of annealing occurs at about 400° C., with a marked change between 700° C. and 750° C., and the change was greatest in the case of the elongation. The influence of time on the effect of annealing was also investigated, and the conclusions reached are: The time of annealing has no influence on the elongation, while the breaking strain is slightly lowered in the case of nickel and more so in hard steel, especially if the time be prolonged, although the result may be influenced by the surface decarburization produced. In all cases the influence of time is very slight, in contradiction to generallyaccepted views.

Silit. R. Perlewitz. (Electrotechn. Zeitschr., xxxiv, 263.)—Silit is a new resistance material made by Gebr. Siemens & Co. It consists essentially of silicon carbide, and is prepared according to methods covered by several patents. The original idea was to use a mixture of silicon and carborundum, together with some organic binding material, but the result of the subsequent processes was to obtain a mixture of some of the silicon carbides. Several instances of the application of the material are given. It can be used as a resistance material at high temperatures, and specially in connection with heating appliances, since it is not affected by temperatures up to 1400° C. Photographs and descriptions are given of various pieces of apparatus in which it is used.

"Cellit": A Non-inflammable Cinematograph Film. C. R. Hennings. (Phot. Journ., liii, 10.)—The celluloid of the ordinary cinematograph film is a compound of nitrocellulose and camphor. It is very combustible, burns rapidly and in such a way as to quickly involve surrounding objects, while the gases evolved include carbon monoxide, nitrogen oxide, and hydrocyanic acid (?), and are highly poisonous. The "cellit" film is practically non-inflammable, and, so far as the adhesion of the emulsion and the suppleness of the base are concerned, the two types of film are identical. Their outward appearance is practically identical. Cellit expands more than the ordinary film in developing, fixing, etc.; but after drying the film assumes its original size, and no shrinkage occurs after several months' storage. The new film is developed, fixed, and washed in the same way as the celluloid film; the pictures are identical and may be colored in a similar way.

Manufacture of Swedish Filter-Paper. G. FORNSTEDT. (Chem. News, cvii, 269.)—Chemical filter-papers are generally made on hand moulds, while those used for technical purposes are manufactured on cylinder machines. The carefully-sorted rags, freed from metallic impurities, are boiled with caustic soda and are preferably bleached in chambers with gaseous chlorine after washing and breaking. The ash in the purified, bleached half-stuff ranges from 0.177 for colored cotton rags down to 0.039 per cent. for new shirt cuttings. The water used must be very pure, but even then it generally introduces 0.02 to 0.05 per cent. of mineral matter into the paper. The beating is regulated according to the rapidity of filtration and fineness of retention desired. For analytical work the paper is extracted with hydrofluoric and hydrochloric acids and washed until the washings do not show any opalescence with silver nitrate. It is then pressed and hung in open sheds, where it is frozen to increase its porosity. If dried before freezing, the desired effect cannot be obtained. Extracted filter-paper contains about 0.015 per cent. of ash. Extreme precautions are taken for the determination of the ash in chemical filter-papers; the chief constituents are silica and calcium, aluminum, and magnesium oxides. The rate of filtration is determined on a paper 6 inches in diameter, through which 6 cubic inches of water at 90° F. (32° C.) should pass in 140 seconds as a maximum to 90 seconds as a minimum.

Liquid Fuel. 'V. B. Lewes. (J. Roy Soc. Arts, lxi, 666, 690, 702.)—This deals with the origin, composition, production, uses, and future supply of petroleum. The author considers that the greater quantity of petroleum has been formed by the slow decomposition of marine vegetation (sea-weeds, etc.). A table from A. Beeby Thompson's "Petroleum Mining" is given, showing the specific gravity and ultimate composition of the various kinds of petroleum,

whilst in another table the specific gravity, flash point, calorific value, and actual evaporative power of various kinds of liquid fuel are given; heavy tar oil is shown to be considerably inferior to a good petroleum fuel oil as a fuel. It is stated that air carburetted with petrol vapor gives good results in the Bone and McCourt system of flameless surface combustion, and experiments have also indicated that fuel oil, finely atomized with air in the correct proportion, and then blown into the tubes containing the granular material, will also prove efficient if the granular material be previously heated.

Stereophotographic Surveying. O. Lemberger. (Eng. News, lxix, 602).—A short history of the development of photographic surveying in Europe, with some examples of photographic location of certain railways, such as the Jungfrau Railway, and examples of topographical surveys. The theory of photogrammetry is briefly explained, and also the theory and practice of stereophotogrammetry. The instruments used for stereophotogrammetry, the stereomicrometer and the stereocomparator, are described, with diagrams of their construction and examples of their practical application. Finally, an instrument called the stereo-autograph is described, which automatically draws a map while an operator manipulates the stereocomparator. Contour lines may be drawn automatically on a map or on a photographic print. Illustrations are given of the use of the instrument for a survey of the Ostler Mountains in the Tyrol. Other possible uses are suggested.

Vulcanization of Rubber. G. Bernstein. (Z. Chem. Ind. Kol., xii, 193, 273.)—Experiments with different kinds of rubber showed that the viscosity is diminished by heating, by mechanical working, and by exposure to ultra-violet rays, and that if the depolymerization indicated by this reduced viscosity be carried to completion, the final result is the same, whatever the agency employed -i.e., solutions of the depolymerized rubber of the same concentration show the same constant viscosity. With Frank and Marckwald's viscosimeter, and using a 3 per cent. solution of rubber in xylene, the final constant viscosity value is 15 seconds. Depolymerization on heating takes place most rapidly between 60° and 85° C., according to the kind of rubber, and these temperature limits are close to the temperature above which, according to Spence, vulcanization occurs most actively. The vulcanization of rubber can be produced by exposing a xylene solution of rubber and sulphur to ultra-violet rays. A xylene solution of a mixture of Hevea plantation rubber with 6 per cent. of sulphur was allowed to evaporate so as to leave a thin film on a transparent quartz plate. This was covered by another quartz plate and exposed on both sides for 40 minutes, at a distance of 15 cm. to the rays from a Heræus lamp of 3 ampères and 110 volts. The film then possessed

the properties of vulcanized rubber and contained 2.56 per cent. of combined sulphur. Other experiments showed that the percentage of combined sulphur increased with the duration of exposure to the rays. The deterioration of vulcanized rubber on exposure to ultra-violet rays, observed by Henri, is considered to be chiefly due to "after-vulcanization." The effect of heat or exposure to ultra-violet rays on sulphur alone or in solution is to polymerize it-i.e., to convert it into a colloidal, insoluble form. Bernstein agrees with Axelrod that the vulcanization of rubber comprises a depolymerization of the rubber, followed by a polymerization of the mixture. If this polymerization of the mixture be of a physical character, it must be accepted that it is due to the adsorption by the depolymerized rubber of the polymerized insoluble sulphur, and this would explain the difficulty of extracting the socalled combined sulphur. It is, however, not yet possible to decide finally between the chemical and physical (adsorption) theories of vulcanization.

Mercury Vapor Lamp. Anon. (Amer. Mach., xxxviii, No. 23, 933.)—The mercury vapor lamp would be ideal were it not so deficient in red rays. It has been found that by operating the lamp at much higher temperatures in a quartz tube the emanation of red rays increases as compared with green and blue rays. But even under these conditions the light it gives does not possess enough red for ordinary commercial purposes. Efforts have been made to find a vapor which will give the desired spectrum. Dr. Wolfke has apparently attained this end by the use of cadmium in the lamp. The vapor of cadmium gives an excess of red light when the temperature of the lamp is raised, but this is corrected by adding a little mercury. It is stated that a lamp of 3800 candle-power uses 620 watts.

Alunite and Kelp as Potash Fertilizers. J. J. SKINNER and A. M. JACKSON. (U. S. Dept. of Agric., Bureau of Soils, Circ. No. 76.)—Raw alunite of 10 per cent. potassium oxide, and ignited alunite of 14.7 per cent. potassium oxide, and dry kelp containing 19.8 per cent. potassium oxide, were added to the soil so as to give 25 to 500 pounds of potash per acre, and were compared with potassium chloride and sulphate. The raw alunite was not so effective as the potassium salts, but the ignited alunite was more effective, the average increase in the crop being about 31 per cent., as compared with about 25 per cent. for potassium sulphate. The kelp gave an increase of about 23 per cent. of the crop, as compared with about 22 per cent. with potassium chloride.



# **JOURNAL**

OF

# THE FRANKLIN INSTITUTE

DEVOTED TO SCIENCE AND THE MECHANIC ARTS

Vol. CLXXVI

OCTOBER, 1913

No. 4

#### KELP AND OTHER SOURCES OF POTASH.\*

BY

#### FRANK K. CAMERON,

Scientist in Soil Laboratory Investigations; in charge Investigations in Soil Physics, Soil Chemistry and Pertilizer Resources, Bureau of Soils, U. S. Department of Agriculture.

Member of the Institute.

#### FERTILIZER PROBLEMS.

The settlement and development of a country is always followed by a change, more or less gradual, from pioneer or "extensive" methods of agriculture to "intensive" methods. Such a change is now taking place in the United States, or at least in many parts of it, for the country covers so vast an area, with widely different physical and socio-economic features in its various regions, that uniform progression is impossible, and one's vision of the whole is quite apt to be occluded by local phenomena. One of the characteristics of intensive cultivation is the coincident employment of the three methods which man's ingenuity has devised for the management of the soil and the production of crops, namely: tillage, crop rotations, and soil amendments, the last being better known in this country as "fertilizers."

Of the many substances which have been found useful in increasing crop production, the experience of the world has shown among the most useful certain substances containing, or

Copyright, 1913, by THE FRANKLIN INSTITUTE.

<sup>\*</sup> Communicated by the Author.

<sup>[</sup>Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.]

"carriers" of, potassium, nitrogen, and phosphorus; and, since these are not obtainable directly by the individual farmer, or require for their best utilization preliminary manipulation, there has grown up, especially in the United States and Europe, a vast business in "commercial fertilizers," which, in spite of many just criticisms and objectionable practices, has, on the whole, been a powerful and beneficient agency in advancing civilization and the development of the nation.

From the national point of view, fertilizers present three problems or groups of problems, namely: (1) the location and extent of raw materials, (2) the manufacture and distribution or sale of the manufactured products, and (3) teaching the farmer what fertilizers to use and when and how to use them. The third group of problems has received an enormous amount of attention from Federal and State agencies, the second group practically none, and the first group but very little until the last two years.

## PHOSPHATES AND NITROGEN CARRIERS.

The phosphate resources of the United States are practically illimitable. There are large deposits of phosphorites or calcium phosphate in Florida, and in Tennessee, as is commonly known. Much phosphate rock still remains in the neighborhood of Charleston, S. C., although the cost of removing the overburden and mining at present has reduced the output. A number of other less important deposits are known, and in the States of Utah, Idaho. Montana, and Wyoming occurs a deposit or group of deposits of high-grade phosphorites greater than all other known deposits in the world, and capable of supplying three times the present demand for at least twelve centuries. As to nitrogen carriers, cotton-seed meal now commands too high a price as a cattle food to be used in fertilizers. The same is true of dried blood and the higher grades of tankage or slaughter-house by-products. The possible supply of ammonia from coke ovens is entirely insufficient, and no natural deposits of nitrates or ammonium salts exist in this country, so far as is now known, sufficient to meet the demands. The more general employment of leguminous crops and green manures will, however, largely meet the need for nitrogen additions to the soil, and the development of practicable methods for the fixation of atmospheric nitrogen as

cyanamide, ammonia, or nitric acid again places an illimitable supply at command.

## POTASH FROM GERMANY.

The case for potassium carriers, however, has exceptionable features. In common with the rest of the world, the United States has been relying on supplies of potash from the Stassfürt mines of Germany. These mines are not inexhaustible, are subject to accident, as in the recent flooding at Jensenitz, when an appreciable percentage of the world's supply of potash disappeared over night, and are, moreover, under the control and at the disposition of a trade rival, who might some time, it is conceivable, become a belligerent rival as well. It is the part of wisdom, therefore, to find and develop an American source of soluble potash salts. Many suggestions to this end have been investigated.

#### MINOR POSSIBLE SOURCES OF POTASH.

Wood ashes are still brought into this country from Canada, but in steadily diminishing quantity, and the amount now is probably less than 4000 tons annually. The domestic supply is practically nil. There is much sawdust and waste lumber produced annually, but scattered over an immense area, and the total possible yield would be probably less than 6000 tons of potassium carbonate. Suint or wool washings have in times past been used in European countries. The wool cut in this country, if all washed, might yield approximately 8000 tons, but the cutting is again widely distributed and could not be profitably worked for potash on a small scale. Waste land in Russia is used to grow sunflowers, which are burnt and the ashes used as a potash fertilizer. It has been suggested that the desert regions of the United States might be utilized, but no suitable plant or methods of handling it are yet in sight. All the brines and salt wells of the country carry some small amounts of potash salts, but a careful investigation has shown conclusively that none now known. can be worked economically for potash salts. In certain burntover areas of Nebraska, and possibly elsewhere in semi-arid areas, are ponds with no outlet or insufficient outlets which have gradually become the depositories of potassium carbonate leached from the surrounding water-shed. Some of these may be of

local value, but none, so far, give any promise of any great importance as sources of potash.

# MAJOR POSSIBLE SOURCES OF POTASH.

The possible sources of potash salts above enumerated are, from a national point of view, merely minor. Recent investigations have established, however, that there are possibly four major sources of potash available in the United States. The mineral alunite, sometimes described as a natural alum, is a basic sulphate of potassium and aluminum. By heating, lixiviating, and subsequent evaporation of the resulting solution, either alum or potassium sulphate can be obtained, as may be desired. The socalled Roman alum of European commerce has long been produced thus in Italy and Spain. Alunite is widely distributed in the United States. But near Marysville, Utah, occurs a very large deposit from which it is probable that a notable quantity of potassium sulphate could be produced annually for many years to come. The deposit has not yet been sufficiently well explored to justify any attempt at quantitative estimates of its possibilities. It is now in private hands, and there is at least a reasonable expectation that it will be producing before long.

In the western and arid portion of the United States are many desert basins which in the course of time have become filled more or less with solid detrita, but which formerly were lakes receiving, in the water flowing into them, soluble potash salts as well as other dissolved material. The aggregate amount of potash salts thus accumulated in some of them must have been very large. It is possible that in the desiccation of such a lake a segregation of potash salts took place and a layer may exist somewhere below the present floor of the basin. Again, the potassium salts may be distributed through the solid fill. A 1000-foot boring in the Carson sink by the United States Geological Survey showed the water to get fresher with increasing depth. This might indicate that the salts, not being distributed, must be segregated at some lower depth. A similar 1200-foot boring by private interests in the Railroad Valley had practically the same experience. Criticisms of these views are, however, that the boring near Fallon was in the old river bed, that the Railroad Valley boring was not in the position of the valley most likely to contain salts, that there is no good reason to assume former enormous depths, that the borings already made

probably reach nearly, if not quite, to the original bottom at these points, and that laboratory experiment as well as field observation indicates that soluble salts would be found, if at all. at or near the present surface. Future investigation, perhaps requiring many years, may be necessary to determine the validity of these conflicting hypotheses. Upwards of two hundred desert basins have now been explored more or less carefully, with one certainly showing the presence of a salt body near the surface containing commercially workable quantities of potash salts. At Searles Lake, San Bernadino County, Cal., there is a playa or mud flat, about 12 square miles in area, and with an average depth somewhere between 40 and 70 feet. This "lake" is a mixture of ordinary soil material and solid salts, including sodium chloride, sodium carbonate (or carbonate and bicarbonatetrona), borax, and possibly potassium chloride, in contact with a mother liquor or brine. In the brine there is about 40 per cent. of soluble salts and approximately 6 per cent. potash. A conservative estimate of the total potassium chloride present would be 4,000,000 tons, and, especially if it is shown, as claimed, that solid potassium chloride is in the salt mixture the total amount may be much in excess of this minimum estimate. potassium chloride may be economically produced from Searles Lake is very probable, if at the same time a market exists for the trona and borax which would be obtained in the separation. Aside from Searles Lake, the possibility of a desert basin producing potash commercially must be admitted. The probability, however, is but a speculation or the proverbial miner's chance.

Enormous quantities of potash feldspar, orthoclase or microcline, exist in this country, and in certain areas leucite, another potassium-carrying silicate. For years chemists have been working to devise methods of extracting the potash from these and similar minerals. It can, of course, be done, and quite readily, in the laboratory. It has, however, come to be recognized that no method has any commercial possibilities which does not, together with the potash or potassium salt, yield also some other salable product. At least one possibility of this kind exists. It has been found in laboratory experiments that powdered or finely-ground feldspar, when substituted for the ordinary clay or shale employed in the manufacture of cement, yields as satisfactory a clinker, and the potash is quantitatively volatilized and can be caught in the stack more or less mixed with the ordinary

flue dust. All the mechanical difficulties in catching the potash have not been satisfactorily worked out as yet, and no commercial production of potash from feldspar yet exists. But the difficulties yet to be surmounted are not formidable, apparently, and potash from feldspar is not only a possibility but a probability of the near future. So far ás can now be seen, however, it must be a by-product. Not all cement mills will produce it, and quite likely it will be recovered as potash,  $K_2O$ , and will command too high a price to be available for fertilizers. On the other hand, there will probably be cases where the flue dust from cement mills will contain sufficient potash to make it valuable as a fertilizer, but where, for one special reason or another, the potash cannot be profitably extracted from the insoluble residue.

From time immemorial sea-weeds have been recognized as having an important manurial value. On many European coasts they are still so used, and on the New England coast of the United States "kelp day" is a festal occasion, when the farmers gather the torn weeds thrown upon the shores in their vicinities and haul them to their farms. In Europe certain of these marine algæ were long gathered and burned, the ashes being known as kelp, a term sometimes applied to the green plants also. These ashes had a considerable value for their iodine content, and the "kelp rights" on the coast of Brittany especially, as well as in certain sections of Ireland, Scotland, Norway, the Hebrides, the Shetlands, and some other vicinities, were of great importance.¹ Besides their remarkable power of abstracting iodine from seawater, sea-weeds generally show another phenomenon, in abstract-

<sup>&</sup>lt;sup>1</sup> In the course of time the iodine business centered in Glasgow, Scotland, and into the hands of a few firms who sent out ships to the points cited above to collect kelp. At present Japan supplies her own needs in iodine from kelp, and has done so since the beginning of her war with Russia. The rest of the world, however, has long been supplied with iodine obtained from the mother liquors resulting from the recrystallization of Chili saltpeter, the control of the business yet remaining in Glasgow. The present price of iodine (about \$1.90 per pound) is an artificial one and could probably be greatly reduced, as it is reported that the possible production in Chili is far in excess of the world's demands. The giant kelps of the Pacific coast all contain iodine, though not in as high proportion as many other sea algæ. They could produce annually a hundred times the average consumption of the United States (about two hundred and fifty tons), but unless new uses for iodine are discovered or extremely cheap methods of extraction are devised there appears to be very little prospect for "iodine from kelp" competing successfully with the Chilian product.

ing relatively large amounts of potassium from the sea, although the latter is very dilute with respect to this element and quite highly concentrated with respect to its chemical analogue sodium. To the large content of potassium is usually attributed the manurial value of sea-weeds, although the easily digestible nitrogen and readily decomposable organic substances they contain probably have much to do with their value.

#### THE GIANT KELPS OF THE PACIFIC COAST.

Introduction.—On the Pacific coast of North America occur a number of different sea-weeds and rock weeds. Three of the brown algae are known locally as the "Giant kelps." These are Nereocystis luetkeana, Macrocystis pyrifera, and Pelagophycus porra. They are characterized by the exceptionally high content of potassium, some five times, on the average, the content of the better-known Atlantic algae.<sup>2</sup> These giant kelps occur in numerous beds or groves, often of great extent, and are beyond question an ample, perennial possible source of potash for the present needs of the United States.

The credit for recognizing the value and importance of the Pacific giant kelps as a source of potassium is due to Mr. David M. Balch,<sup>3</sup> of Coronado Beach, who in several journal notices as well as patents called attention not alone to the high content of potassium in these plants, established by careful analysis, but to their vast aggregate amount; and pointed out possible methods

<sup>&</sup>lt;sup>2</sup> That high content of potassium may be found in other algæ is, of course, recognized. A sample of "Sea lettuce" gathered by Captain Crandall near Point Loma, and analyzed recently by Dindemuth and Merz, contained 30 per cent. potash (K<sub>2</sub>O), or 47.4 per cent. potassium chloride, out of 57.1 per cent. total soluble salts. There were also present in the dried sample 32.8 per cent. organic matter and 1.7 per cent. nitrogen.

<sup>&</sup>lt;sup>a</sup> Mr. Balch's principal publication appeared in the Journal of Industrial and Engineering Chemistry, in 1909, vol. i, p. 777.

His work on the Pacific Kelps, the labors of years, has as yet brought him neither the financial nor scientific rewards its importance so richly merits. Advanced years and uncertain health have caused him to cease active work on this subject, although his interest is yet as keen as ever, as the writer can testify from recent personal interviews and an active correspondence. It is a privilege to have this opportunity of recording appreciation for and calling attention to the amiable personality and important public services of this pioneer in the development of a great natural resource of the nation, and especially of his adopted State of California.

of manipulation for their commercial exploitation. Balch's work, however, failed to attract attention. Meanwhile, working under a process devised by the late Dr. Firmin, of San Diego, The Coronado Chemical Company was attempting to prepare a product or products by fusing kelp and natural phosphorites, lixiviating the melt, and subsequent crystallization from the resulting solution. The process failed to develop commercial possibilities and has been abandoned. Other more or less desultory efforts to utilize kelp on a commercial scale were made from time to time. For instance, Mr. Andrews, of San Diego, prepared a beautiful paper from it, and serious consideration was at one time given to a plan to prepare fibre from the yucca very common on the arid deserts of Southern California, to be worked into paper, with kelp as a raw material for the binder and filler.

Samples of kelp and potassium chloride prepared therefrom by Mr. Balch were called to the writer's attention and examined in September, 1910. As nothing definite was known at that time regarding the extent of these marine growths, no further attention was given to the matter, especially as neither money, authority, nor opportunity then existed for an investigation. Some time later, when the investigation of the fertilizer resources of the United States had been inaugurated, the results of this examination were recalled, and steps were taken to make a recognizance survey of the extent of the kelp groves and to collect representative samples for analysis and confirmation of Balch's data. During the summer of 1911 field observations were made by Prof. Geo. B. Rigg on Puget Sound, by Prof. Frank M. McFarland of the coast from the Golden Gate to Point Sur, and by Captain W. C. Crandall of the coast from Cape Conception to Point Loma. Laboratory investigations at Washington of the samples collected, together with these field studies, showed the giant kelps of the Pacific coast<sup>5</sup> to be an ample and satisfactory possible

<sup>\*</sup>One of the most interesting products obtained from kelp is a conserve much resembling candied citron, which Prof. T. C. Frye, and C. E. Magnuson, of Washington University, Scattle, prepare by leaching out the potassium and sodium salts and then steeping the residue in cane-sugar solution containing lemon or any other desired flavoring. The product coming from the sea, being first made in Seattle and much resembling citron, has been named "Seatron." It has apparently great merits and should some time find a good market.

<sup>&</sup>lt;sup>6</sup> For details of this work, see Senate Document No. 190, Sixty-second Congress, Second Session, 1912.

source of potash. The work was continued in 1912, and, as a result, working maps have been prepared of kelp groves aggregating 230 square miles, from and including the United States shore line of Puget Sound to the Cedros Islands, Mexico. A large number of samples were collected and analyzed, and observations made having an importance for the development of a "potash from kelp" industry. This present year two parties are at work locating and determining the extent and important characteristics of the kelp along the Alaskan shore line. A third party is investigating on the ground the possibilities of developing a combined fish scrap and kelp industry on Puget Sound and in Alaska, and important laboratory investigations are in progress at Washington, D. C. Observations are also being made at La Jolla and Point Firmin, Cal., and at Friday Harbor, Wash., on factors in the life-history of these algæ of importance to their utilization commercially, and more especially to the effects upon the stand of cutting over and harvesting kelp.

Distribution of Kelp.—In the Puget Sound region and as far south as Point Sur, on the California coast, the principal kelp is the nereocystis. Macrocystis also occurs, usually in a band outside the nereocystis and, of course, in deeper water. From Point Sur southwards nereocystis practically disappears. The macrocystis occurs in large groves or beds, often several miles in extent and from a few yards to two or more miles in width. Along the outer edge of the macrocystis, in scattered groups or individual plants, occurs the pelagophycus. The pelagophycus has probably the highest content of potassium, but does not occur in sufficient quantities to give it any great commercial importance.<sup>6</sup>

Conditions for Growth.—The conditions for growth for all three species of giant kelps are similar in that there must be a rocky bottom and a continuous and considerable movement of the water. The kelps have no root system as land plants in the sense of a mechanism for absorbing a solution of substances needed for their metabolism; but they have a group of tentacle-like branches, much resembling in outward appearance a root system, known as the "holdfast," which surrounds a rock, pebble, or other heavy and more or less permanent object, and thus anchors the plant. Inasmuch as the plants often grow to a very

<sup>•</sup> Pelagophycus is the kelp employed in the manufacture of curios familiar to tourists in Southern California. The business is but a minor one, aggregating a few thousand dollars annually.

large size, much oxygen and carbon dioxide are required by it, and, being submerged, it must obtain these constituents from the supply dissolved in the sea-water. Consequently new masses of water must be continually supplied. In the Puget Sound region and along the island-studded coast of Alaska nereocystis is likely to be found wherever there is a fairly rapid tide movement over a rocky bottom. The depth of water may be only two or three feet up to several fathoms. Macrocystis is found on exposed coasts where there is a continual swell. It grows at three fathoms and less in small patches, but the larger groves are usually at depths of from six fathoms at the shore side to ten

Fig. 1.



A holdfast of nereocystis.

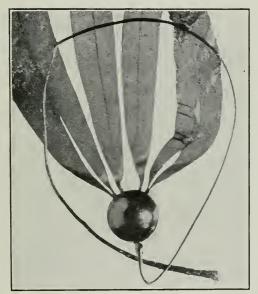
fathoms at the seaside. Pelagophycus is usually found at depths of from eight to fourteen fathoms.

The giant kelp groves are what a forester would call practically pure stands. They are all chlorophylous plants with leaves floating on the surface, for which they are provided with special floating devices, the pneumatocysts. Their tissues are practically fibreless, but quite turgid, and lose from 80 to 85 per cent. when dried. Nereocystis has a long, hollow stipe from the holdfast to the pneumatocyst, which is a hollow, sphere-like contrivance about six inches, more or less, in diameter, with a fleshy wall of perhaps an inch or less in thickness. This bulb floats with the tide, and from it stream out a leaf or leaves relatively narrow,

but some leaves of great length. It is sometimes known locally as ribbon kelp, sometimes as bull kelp.

Pelagophycus is like nereocystis in having a long, hollow stipe from the holdfast, ending in a spherical pneumatocyst. But the pneumatocyst of pelagophycus is two or more times wider than with the nereocystis, and from it spring horn-like stipes, ending in leaves. Because of the horn-like branches this kelp is commonly known as elk kelp; sometimes also it is called bull





Young nereocystis plant, showing pneumatocyst and basal splitting of leaves.

kelp, probably from confusion with nereocystis, because of the prominence of the spherical pneumatocyst on the end of a long stipe in both plants.

Macrocystis has a somewhat different manner of growth and quite a different appearance. From the holdfast spring a number of stipes, often branched and usually from 80 to 100 feet in length. Along these stipes spring fronds, each leaf carrying at its base and connecting it to the stipe a small, hollow

<sup>&</sup>lt;sup>7</sup> Much greater lengths are by no means unusual, and the enormous length of 1000 feet has been reported.

pneumatocyst which floats it. The leaf would probably average 12 to 14 inches in length, three to four inches at its widest, and is serrated. The pneumatocyst is roughly ovoid in shape, about two inches in length and three-fourths of an inch in diameter of widest cross section.

Period of Growth.—Nereocystis is an annual. It is propagated by spores which are developed in certain spots or areas





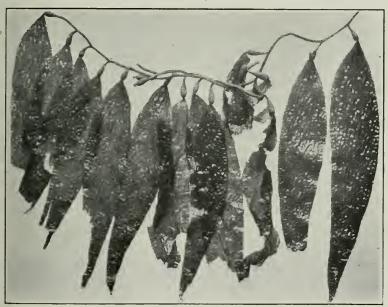
Rock near Turn Island at low tide. The two men are holding a nereocystis plant. The rocks on which they are standing are covered with alaria.

on the leaf and are ripe, in the Puget Sound region, about the middle of July. If cutting of the groves becomes extensive it may be desirable to establish a closed season until July 15 or perhaps a week or two later, to prevent a "killing out" of the groves. The other alternative is to permit early cutting, but under supervision and control, so that a fair percentage of vigorous plants may mature to "reseed" the grove. Until further and more definite knowledge of the life-history of the plant is at hand, and certainly until after a kelp industry is

actually established, it is of doubtful wisdom to formulate or enact any restrictive legislation, although such has been proposed.

Macrocystis has a life-history certainly longer than a calendar year, and is probably a perennial. It also grows from spores, but these develop, generally, on leaves at considerable depths below the surface. It seems altogether improbable that cutting over the groves of this plant, even to depths of two fathoms, could produce any permanent injury. It is popularly supposed that a cut macrocystis stipe will continue to grow, and that a cut-over





Macrocystis pyrifera from Southern California.

grove will be restored to its former condition in from 40 to 60 days. Recent observations made specifically to obtain information on this point appear to show clearly that when a stipe of macrocystis is cut decay sets in at the injured surface and progresses slowly toward the holdfast. Because of the mechanical stimulation, or from some unknown reason, however, cutting induces new stipes to be sent out from the holdfast, or a branching of the old stipes, so that an effect is produced on the plant

akin to or similar to the well-known "stooling" of wheat. Be the explanation what it may, areas cut over near Point Loma and Point Firmin were less than a year later much heavier and thicker in growth.

Loss of Potash from Dead Kelp.—Kelp, when cut and allowed to lie in the water, soon loses its high content of potash. Drift kelp contains but little. It is certain that the leaching commences at once after cutting, and that various schemes of harvesting which have been proposed, such as towing the floating kelp in nets or allowing it to wash ashore in the surf and then gathering it on the beach, are fundamentally incorrect in principle, and the kelp should be removed from the sea and drained as soon as practicable after it is cut. Moreover, even though lying in a strong brine, as in sea-water, the cut kelp soon shows evidences of decay, and large masses of putrescent kelp are neither easy nor pleasant to handle.

To obtain some definite evidence of the rate at which the potassium chloride leaches from the cut kelp, Captain Crandall cut samples of kelp and hung them overboard during a cruise of the yacht *Agazzi*, of the Scripps Biological Institute, La Jolla, Cal., cutting out sub-samples from the leaching kelp from time to time, and sending them to Washington. The samples were in somewhat putrescent state when they arrived, but were dried as quickly as possible and then analyzed by Messrs. Lindemuth and Merz, with the results given in Tables I and II.

TABLE I.

Analyses of Kelp Gathered near Coronados Island, April 16, 1913, 2:30
p.m., and Remaining in the Water for Various Lengths of Time.

Date	Time	K <sub>2</sub> O, Per cent.	Soluble salts, Per cent.	Organic matter, Per cent.		Nitrogen, Per cent.
April 16	2:30 P.M.	12.48	31.46	65.38	3.16	0.98
April 16	2:30 P.M.	13.47	31 26	65.98	2.76	.79
April 16	5:30 P.M.	15.56	34.00	62.38	3.62	.95
April 16	8:30 Р.М.	17.30	38.26	58.66	3.08	I.00
April 17	4:30 A.M.	17.64	38.30	58.30	3.40	1.07
April 17	7:30 A.M.	13.35	31.96	54.96	3.08	.83
April 17	IO:30 A.M.	10.74	26.36	70.66	2.98	.90
April 161	2:30 P.M.	18.28	36.78	60.86	2.36	.51
April 162	2:30 P.M.	9.90	25.94	70.18	3.88	.84
	¹ Stems o	nly.	<sup>2</sup> Leaves o	nly.	_	

TABLE II.

ANALYSES OF KELP GATHERED NEAR POINT LOMA, CALIFORNIA, APRIL 18, 1913.

4 P.M., AND REMAINING IN THE WATER FOR VARIOUS LENGTHS OF TIME.

Date	Time	K₂O, Per cent.	Soluble salts, Per cent.	Organic matter, Per cent.	Ash, Per cent.	Nitrogen Per cent
April 18	4 P.M.	15.82	40.88	47 - 32	11.80	2.77
April 18	7:30 P.M.	13.43	34.82	56.54	8.64	2,66
April 19	7:30 A.M.	14.96	37.66	52.76	9.58	2.40
April 19	10:30 A.M.	13.05	34.34	60.12	5 · 54	1.77
April 19	1:30 P.M.	11.00	30.22	62.52	7.26	1.85
April 19	4.30 P.M.	11.59	30.52	59.92	9.56	2.10
April 19	7:30 P.M.	13.68	38.94	50.56	10.50	2.22
April 20	7:30 A.M.	10.31	27.84	62.38	9.78	1.97
April 20	10:30 A.M.	16.39	38.78	53.30	7.92	2.22
April 20	I:30 P.M.	11.77	32.44	60.54	7.02	1.99
April 20	4:30 P.M.	16.69	39.72	54.22	5.96	1.79
April 20	7:30 P.M.	15.77	40.80	45.88	13.32	2.29
April 21	7:30 A.M.	16.74	42.58	45.36	12.06	2.49
April 21	10:30 A.M.	16.75	38.64	55.28	6.08	1.91
April 21	4:30 P.M.	14.67	35.58	58.12	6.30	1.88
April 21	7:30 P.M.	12.61	34.74	55.46	9.80	2.66
April 22	7:30 A.M.	15.54	40.84	48.92	10.24	2.47
April 22	10:30 A.M.	17.62	41.42	49.48	9.10	2.16
April 22	I:30 P.M.	17.03	42.44	44.50	13.06	2.28
April 22	4.30 P.M.	15.61	37.80	54.42	7.78	2.16
April 22	7:30 P.M.	20.28	46.28	43.96	9.76	2.12
April 23	7:30 A.M.	15.72	38.80	51.44	9.76	2.26
April 24	7:30 A.M.	15.60	39.24	48.74	12.02	2.57
April 23	-	15.27	34.52	57 - 42	8.06	1.80

These results show no consistent trend, and it appears probable that for some time after cutting and until the individual cells of the plant tissues have died the loss of potassium from the cut kelp is relatively slow.

Drying of Kelp.—All the giant kelps, when cut and exposed to the air, lose water quite readily. The tissue shrivels and on the surface appears an incrustation or efflorescence of the salt mixture, mainly potassium and sodium chlorides, the former predominating decidedly. This salt mixture is easily shaken off the dried plant.<sup>8</sup> But, although kelp, when freely exposed to the air, loses water and dries quickly, green kelp, when allowed to lie in heavy wet masses, quickly packs to a sticky, slimy mass of

It is said that nereocystis freshly cut and almost immediately dried in an oven on a fairly large scale, in some practical experiments made at Port Townsend, Wash., did not exhibit any efflorescence nor lose any salt when shaken.

putrescent material, with a most offensive odor and most attractive to flies.

Experience has apparently demonstrated that in commercial practice, except possibly on the Mexican coast line, it will be desirable to dry the kelp by artificial means. Various schemes for this purpose have been proposed, but apparently the most practical and efficient would be a rotary cylinder, with lengthwise baffle plates, to break up the kelp masses, the cylinders set at a slant and a current of hot dry air being passed through it. The kelp, cut into short lengths, is fed by a hopper into the upper end and the dried product falling from the lower end removed by endless conveyor or any appropriate means. The whole device is quite similar to the familiar ordinary cement kiln or modern lime furnace, except that a current of hot dry air, instead of a naked flame, is blown through. Similar dryers are used for desiccating fish scrap and such like materials, dry porous rock, and even for evaporating brines. Dryers of this type which can be reasonably expected to handle kelp very efficiently are now on the market and can be procured at very reasonable prices.

Composition of Kclp.—The composition of the kelp tissue is not at all satisfactorily known. It probably differs considerably with different species and varieties. A few definite substances have been isolated, and a number of "algins" and "alginic acids," etc., for whose definite existence there is no satisfactory evidence, although some of the properties of the actual masses of these hypothetical individuals are very interesting and possibly of considerable technical importance. Confining attention, however, to the fertilizer possibilities, a considerable mass of data

has now been accumulated regarding the giant kelp.

The composition of the giant kelps as regards their fertilizer constituents has been determined, at least approximately, now by numerous analyses by Balch, Turrentine, Lindemuth, and Parker. In Tables III, IV, and V are given results obtained by Turrentine or Lindemuth and Parker on samples of ovendried kelp (105° C.) which appeared to be fair average specimens and selected otherwise only as regards their distribution along the coast. The averages in these tables do not, however, accord very closely with those obtained by Parker and Lindemuth<sup>9</sup> from

<sup>\*</sup> Journal of Industrial and Engineering Chemistry, 5, 287 (1913).

TABLE III.

Composition of Nereocystis.

Location	K <sub>2</sub> O. Per cent.	I, Per cent.	N, Per cent.	Organic matter, Per cent.
Fresh Water Bay, Puget Sound	18.04 17.61 31.62 16.92 17.05 17.32 16.20 16.50 16.72	0.23 .24 .25 .20 .24 .28 .19 .30 .20	2.26 2.21 1.21 2.57 2.71 2.53 2.54 2.21 1.46	51.13 51.11 33.15 51.16 51.67 50.12 52.14 37.40 39.02
San Juan County, Wash	25.70 13.30 23.00 16.20	.08 .15 .17	I.29 2.52 I.32 2.32	41.80 61.50 46.20 35.30
Point Arena, Cal	16.72 20.62	. 13 . 15	2.22 2.25	53.56 51.42
Bay of Monterey, Cal	16.96 23.82 21.70	. 20 . 17 . 18	2.15 2.41 1.58	57.25 47.26 50.20
Point Pinos, Cal	19.40 26.10	.12 .15	I.70 I.12	53.00 40.60
Cayucos, Cal	20.83	.24	1.93	47.86
Average	19.63	0.19	2.02	47.75

a consideration of all the existing analytical data, including good, bad, and indifferent specimens. Their averages are probably more reliable approximations, and from them the following conclusions may be drawn.

- (1) No definite quantitative relations exist between the different constituents of kelp.
- (2) The potassium content of nereocystis is greater than that of macrocystis.
- (3) The potassium content of northern kelp is higher than that of the southern kelp.
- (4) There is no positive difference in iodine content between northern and southern kelps.

So far as results obtained are available, the following conclusions also seem justified:

(5) The proximity of the mouth of a fresh-water stream has no appreciable effect on the potash and nitrogen content of kelp.

TABLE IV.

Composition of Macrocystis.

Location	K <sub>2</sub> O, Per cent.	I, Per cent.	N, Per cent.	Organic matter, Per cent.
Low Point, Wash	12.80	0.23	1.37	59.40
Neah Bay, Wash	19.60	.20	1.81	51.50
Pillar Point, Cal	17.26	. 15	2.18	58.14
	27.66	. 14	I.00	41.04
Santa Cruz, Cal	16.44	.24	2.16	59.80
Monterey Bay, Cal	18.30	. 26	2.32	57.00
	12.38	. 18	2.II	68.80
Point Aulon, Cal	23.00	. 32	1.83	51.20
Point San Luis, Cal	8.62	.14	2.35	68.26
Rocky Point, Cal	9.35	.25	2.72	73.06
Point Conception, Cal	14.17	.24	2.15	62.95
San Miguel Island	16.40	. 29	1.54	50.60
Santa Cruz Island	17.40	. 32	1.57	49.40
Anacapa Island	12.60	. 26	.95	64.40
Cape Quemada, Cal	14.10	.29	.90	63.50
Goleta Point, Cal	16.70	. 17	1.00	56.70
Point Las Pitos, Cal	12.30	.20	.98	66.20
La Jolla Point, Cal	13.60	. 38	1.04	64.40
Point Medanos, Cal	13.40	.23	.74	62.90
Point Loma, Cal	15.70	. 15	.90	60.90
Average	15.59	0.23	1.58	59.51

TABLE V.

Composition of Pelagophycus.

Location	K <sub>2</sub> O, Per cent.	I, Per cent.	N. Per cent.	Organic matter, Per cent.
Point Firmin, Cal	12.10	0.27	1.10	65.50
San Nicolas, Cal	19.5 15.60	.50	1.01 1.63	52.40 56.20
San Clement Island, Cal	29.90 22.40	·35	· 53 . 69	36.40 48.40
Average	19.90	0.36	.99	51.78

(6) There are no essential differences between the potash and nitrogen content of fronds and stipes.

(7) There are no essential differences in the potash and nitrogen content of old and young plants. 10 Further data on

<sup>&</sup>lt;sup>30</sup> Some analyses reported recently show that very young nereocystis contained less than 20 per cent. potassium chloride, but nearly 5 per cent. nitrogen.

this point are, however, very desirable, as well as possible variations with the season.

Kelp as a Fertilizer.—That freshly-cut kelp has a high value as a manure is unquestionable, as the experience of hundreds of years in various parts of the world testifies. That such material could have any great importance in commerce, however, is impossible, for various reasons, more or less obvious, of which one is sufficient, namely, that it can not be made profitable to pay the freight on the large proportion of water in the kelp.

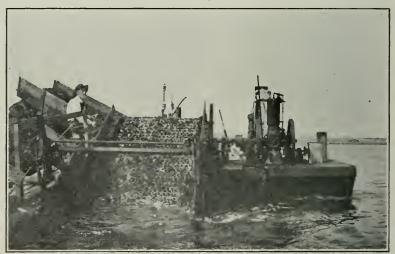
It appears that Balch gave considerable attention to this matter some years ago, and concluded that air-dried kelp, or material dried at ordinary oven temperatures, would not be suitable fertilizer. On the other hand, he concluded that kelp parched at temperatures of 200° C. to 240° C. underwent such changes that it could be satisfactorily used. This product he called "saline humus" and took out a patent (No. 771760, October 4, 1904) covering it. He described it as follows: "The material in this state,—i.c., parched and ground,—can be marketed, per se, as a very cheap and efficient fertilizer, being rich in potassium salts and containing calcium and magnesium, both as phosphates and in combination with organic acids. The material also contains nitrogenous substances, which, as they decompose, yield ammonia and other compounds of nitrogen to the soil. It is also possible to mix this product with the various substances required by certain crops in the manufacture of a number of special fertilizers." Balch, however, clearly considered that the best utilization of kelp is to subject it to destructive distillation, recovering potassium chloride from the char, and obtaining at the same time various salable products.

As a "paper proposition" Balch's final suggestion leaves room for arguments as to details only. Practically, however, it appears altogether probable that the most desirable utilization of the giant kelps at this time is to dry them, and possibly to grind the dried product, depending on the condition of the product coming from the kiln. The material thus obtained is in an ideal mechanical condition for use as a fertilizer, either to be used directly or to be mixed with other materials.<sup>11</sup> Such samples

<sup>&</sup>lt;sup>11</sup> For a comparison of the manurial value of dried kelp with ordinary potash salts see Skinner and Jackson, Circ. No. 76, Bureau of Soils, U. S. Dept. Agric., 1913.

have repeatedly been made in the laboratory, and have been tested with regard to its value as a fertilizer. The products so obtained have averaged above 15 per cent. potash  $(K_2O)$  and 2 per cent. nitrogen, the nereocystis sample running higher than those prepared from macrocystis. There can be no reasonable doubt that the material, if supplied in large enough lots and promptly to order, will find a ready market. The preparation of pure potassium chloride, iodine, gums, etc., may be practicable, and may ultimately prove more profitable. This is for the future to

Fig. 5.



End view of kelp harvester, Pacific Kelp Mulch Company, Los Angeles, Cal.

show. At present, however, and for the prompt establishment of a kelp business the preparation and sale of dried kelp offers by far the best opportunities.

Harvesting of Kelp.—Until recently the harvesting of the kelp on a sufficiently large scale to make it a commercial possibility appeared the chief stumbling-block. Numerous devices have been proposed and several tried out experimentally. By far the greater number of these proposed kelp cutters employed the well-known principle of the ordinary horse-drawn hay-mowing machine to be found on every farm. This principle is employed in a practicable machine now operating on the kelp groves near

Point Firmin, and the problem of cutting and harvesting the kelp can safely be said to be solved, although undoubtedly improvements and refinements of detail and technic are not only possible but surely to come with increasing experience. The device in actual practice consists of a flat decked barge. Over one end projects an endless belt device 16 feet wide and extending into the water to a depth of four feet or a little more. At the submerged end of this belt is a horizontal scythe blade, and at each end of the horizontal blade a perpendicular blade, each blade fitted with a gear device to give it a cutting motion

Fig 6.



Kelp harvester. Hopper.

with a stroke of about four inches. The inboard end of the endless belt extends over a hopper, at the bottom of which is a set of revolving blades, of the type of an ordinary lawn mower. Below these revolving blades is the end of a belt conveyor on a pivoted frame and extending over the side of the barge. The whole device is mounted on appropriate frames and driven by a gasoline engine. In action an undecked towing barge is brought beside the cutter barge. A launch behind them pushes the barges through the kelp groves at a pace of about four miles per hour. The kelp as it is cut falls on the endless belt, is carried over the hopper, through which it falls, is cut into six-inch lengths and conveyed over the side to the towing barge. Usually four men are employed—one on the launch, a second to watch the cutting and with a boat-hook ward off logs and similar floating materials sometimes entangled in the kelp. The third man attends to the loading and distribution of the kelp in the towing barge, and a fourth looks after the engine and running gear.

Cost of Harvesting Kelp.—This cutter has been in actual operation for upwards of a year, cutting kelp intermittently, but in the aggregate has harvested more than 2500 tons. Its opera-





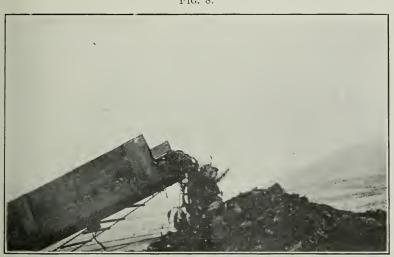
Kelp harvester. Hopper and second conveyor.

tion is a very impressive and convincing sight, of which some idea can be obtained from the accompanying photographs.<sup>12</sup> To give the cost of harvesting green kelp is a difficult matter for several reasons. The existing data are limited. Definite figures have been obtained for only one locality and for only one equipment; and such definite data as the writer has were acquired in confidence. Disregarding earlier estimates, in the light of

<sup>&</sup>lt;sup>12</sup> Acknowledgment is here made of the courtesy of Mr. George H. Ennis, of Los Angeles, Cal., in putting these photographs of a kelp harvester at the writer's disposal.

observations made this past spring, the writer estimated that green kelp could be harvested for 60 cents per ton, with an equipment consisting of: one cutter, cutting 500 tons per day of eight hours' actual cutting; two towing barges with 85 tons capacity each; two launches; and a total crew of six men. This price includes landing. Subsequently, figures were seen taken from actual practice which indicated that wet kelp from the Point Firmin groves could be landed at San Pedro or Long Beach at not to exceed 20 cents per ton. This figure would, of course, have to be modified for longer hauls or different equip-

Fig. 8.



Kelp falling from second conveyor into towing barge.

ments, but for the sake of arguments and tentative calculations it will probably be safe and conservative to estimate the cost of harvesting at 40 cents per ton of wet kelp. The cost of harvesting and marketing dried kelp as a fertilizer can now be estimated with a sufficiently fair approach to accuracy to determine at least the commercial possibilities. It is believed the following figures are all conservative, and the resultant is probably an underestimate. It will be convenient to make these estimates for a plant with a cutting barge, two towing barges, two launches, employing six men, and with a dryer and storage warehouse ashore employing three additional men.

Vol. CLXXVI, No. 1054-27

Plant site	1 /
Dryer, engine and mechanical equipment	4,000
Warehouse	5,000
Cutter and barge	4,000
Two towing barges at \$4000 each	8,000
Two launches at \$2000 each	4,000
Working capital	25,000
-	
	\$60,000

Fig. 9.



Kelp on towing barge.

Five hundred tons of green kelp is equivalent to 75 tons of dried kelp.

Harvesting Drying Sacking Overhead, interest and deterioration	45 <b>7</b> 5
Cost per ton of dried kelp	\$370

Allowing 15 per cent. potash at 65 cents per unit and 2 per cent. nitrogen at \$2.50 per unit, then the selling price of dried kelp per ton is \$14.75. Net profit if sold at point of shipment should be \$9.82. Assuming 200 working days a year on the average, a fair assumption on the Southern Californian coast,

there should be an annual production of 15,000 tons, worth approximately \$147,000, a return of over 245 per cent. on the investment. If, however, there must be deducted freight and handling charges to the Atlantic seaboard, Hawaii, or Japan, to ship to Charleston or Baltimore *via* the Panama Canal, \$5.50 per ton ought to be a fair estimate, which would leave \$64,800, or 108 per cent. profit.

For the Puget Sound region it is to be doubted if a cutting season of over 100 days can be claimed. The cost of equipment would be about the same, but the other figures would have to be



Fig. 10.

Landing kelp at factory.

altered somewhat. It is altogether probable, however, that a return of at least 50 per cent. on the investment could be safely estimated.

While it is, of course, possible that a profitable business might be built up on a smaller scale than here assumed, and with a plant working intermittently, the prospects of a sound business would not be particularly alluring and would have no national importance. Comparatively little fertilizer of any kind is now used on the Pacific coast; and there seems to be a decided preference for potassium sulphate rather than the chloride. That the use of fertilizers will rapidly increase, and that with the increase the

value of dried ground kelp will be appreciated, is altogether probable; but for the present it is to the manufacturer of mixed fertilizers that one must look for the main market. The tonnage of fertilizers sold in the United States is steadily increasing, and at the same time the average grade of mixed fertilizers is steadily getting higher. The mixer at present makes less profit on the potash he puts in his goods, probably, than on any other constituent. Concession to him in price of his potash, and the fact that kelp is a carrier of nitrogen as well, would attract his attention, if he were assured of the ability to secure reasonably prompt delivery in large lots. For these reasons a fair margin of working capital, a storage capacity of several thousand tons, and a production of several hundred tons a week are considered necessary to insure a stable business.

Practicable Production of Potash from Kelp.—As to the number of units of the size here indicated, which could be profitably established, it is impossible to estimate with any approach to accuracy, and an opinion only can be offered. The consumption of potash in the United States at the present time. expressed in terms of the chloride, is approximately 841,000 tons. About 27 per cent, of the potash in the salts from Germany is in lowgrade material whose importation would probably be much curtailed with the introduction of kelp potash on the Atlantic seaboard, although it is doubtful if the importation of high-grade goods would be much affected, barring the introduction of factors not now determining conditions. Taking everything into consideration, a growing market in this country, both East and West, and the probability of a trade with Hawaii, Japan, and the West Indies, it seems safe to estimate at least 300,000 tons of potassium chloride or about a million tons of dried kelp could be marketed per annum if it were now available. produce this amount would require, according to the above estimates, 66 units with a capital investment of \$4,000,000, and this in the face of a growing market.

Preparation of Pure Potassium Chloride.—The separation of pure potassium chloride from kelp is perfectly possible, so far as the theory and the technical features of the problem are concerned—at least on paper. Theoretically, it should be a very simple problem to add sufficient water to the kelp to dissolve the potassium chloride which would also be sufficient to dissolve all

the sodium chloride and to filter off the resultant solution. The residue when dried would contain 4 or 5 per cent. of nitrogen and should be worth \$10 to \$15 as a fertilizer and probably more as a cattle food, while the pure potassium chloride from the evaporated solution would be worth about \$40 a ton. That is, the separation would increase the selling value of a ton of dried kelp from \$14.75 to \$25 or more, an attractive advance.

As a matter of fact, however, the freshly-cut kelp already contains far more than sufficient water to dissolve all the salts present. Unfortunately, moreover, the absence of fibre and the tissue structure of kelp is such that anything approaching a clean separation of salt and organic residue, by filtration, percolation, or even diffusion methods, seems impossible, or at least so difficult and consequently expensive as to be impracticable. On the other hand, a fair separation of the effloresced salts from the organic residue can be effected by agitating the dried kelp on a sieve.

The further separation of the potassium chloride from sodium chloride can be effected in several ways. The most satisfactory one would probably be to treat with water at two different temperatures, as, for instance, the boiling temperature of water, 100° C., and ordinary room temperature, say 25° C. The concentrations of the "constant solutions" for this salt pair at various temperatures have been determined by Precht and Witt. <sup>13</sup> For the sake of argument let it be assumed that the salt mixture contains 60 per cent. potassium chloride and 40 per cent. sodium chloride, an assumption apparently justified by laboratory experience. Further, using rounded figures as sufficiently accurate for the present purposes, assume the composition of the solution to be:

For the sake of simplicity the condition is imposed also that the mass of water remains or is kept constant. Commencing, then, with a thousand pounds of water at 25° and adding 725 pounds of the salt mixture, a brine will be formed, but at the same time there will be left a solid residue of 275 pounds of potassium chloride.

If, now, the solution be decanted or filtered from the residue,

<sup>&</sup>lt;sup>18</sup> Ber., 14, 1667 (1881).

heated to 100° C., and 317 pounds of salt mixture added, 157 pounds solid sodium chloride will be formed.

Again decanting, cooling the brine to 25° C. and adding now 75 pounds of salt mixture, results in the formation of 235 pounds of solid potassium chloride. From this point on, each time the mother liquor is raised to 100° C. with the addition of 317 pounds of the salt mixture, 157 pounds of pure solid sodium chloride will be formed; and each time the mother liquor is cooled to 25° C. with the addition of 75 pounds of salt mixture, 235 pounds of pure solid potassium chloride is obtained. The two processes form a cycle involving: (1) two decantrations or filtrations, (2) one lifting of a 30 per cent. (approximately) brine or two pumpings, one in each direction, and (3) the heating of a 30 per cent. brine to 100° C., besides (4) several shovellings of salt mixture and divers minor mechanical operations.

Comparative Values of Sifted and Unsifted Kelp.—If it be assumed that in shaking the effloresced salt from the kelp the organic residue remaining is 50 per cent. of the total and that 20 per cent. as sodium chloride and 30 per cent. as potassium chloride is in the salt mix, then it will require three and one-third tons of dry kelp to produce one ton of potassium chloride. At \$3.93 per ton for the dry kelp a ton of potassium would cost in the raw material \$13.10. The cost of the heating and pumping operations, in the cycle above outlined, would cost less than 5 cents per ton of brine, or about 50 cents a ton of potassium chloride. Allowing, then, for one ton of potassium chloride:

Raw material  Heating and pumping  Bagging  Labor  Overhead, depreciation, etc.	\$13.10 .50 1.00 .20 1.00 \$15.80
Cost	40.00

The organic residue, amounting to one and two-third tons, with a nitrogen content of 4 per cent., would be worth \$10.65

(at \$2.50 per unit for nitrogen). Allowing nothing for the sodium chloride as balancing the cost of the sifting, then three and one-third tons of dry kelp with the potassium chloride sifted out would bring \$34.87, or one ton of dry kelp would bring, after sifting and recrystallization, \$10.46, against \$9.82 when not further treated. In other words, there would be apparent gain if the products were sold at the point of manufacture. But it is to be noted that there is a saving of 20 per cent. in freight, due to the elimination of sodium chloride, so that the profits at Baltimore or Charleston would appear to be, respectively, \$4.32 and \$6.06 in favor of the sifted and recrystallized product. If the organic residue were sold on the Pacific coast as a cattle food and the potassium chloride alone shipped to the Atlantic seaboard, the margin would become even greater, and the operations of sifting and recrystallizing would show sufficient advantage to justify the kelp being handled in that way.

But the separation of organic residue from the salt, so far as laboratory experience goes, is very far from being as complete as assumed in the foregoing calculations, and there is as yet no factory experience involving the handling of large masses of dried kelp from which even an intelligent guess can be made. At present it would appear to be much sounder business policy to depend on the marketing of the dried kelp without further treatment, unless, indeed, it be found desirable to pass it through a grinder, a comparatively inexpensive operation with such material. On the other hand, it is to be noted that the procedure of crystallizing at alternate temperatures, first the sodium chloride and then the potassium chloride, would finally concentrate a high percentage of potassium iodide in the mother liquor, so high that it could be easily recovered and add to the value of the process.

Existing Kelp Companies.—Since attention has been directed to the commercial possibilities of giant kelps there have been a number of companies proposed for their exploitation. Some have been perfectly legitimate, straightforward enterprises, others merely stock-jobbing propositions, and some, the most objectionable "wild-cat" schemes. Of the proposed companies now before the public, four have given tangible evidences of good faith by actual investment in equipment. The Pacific Products

Company of San Pedro, Cal., with a capital of \$100,000, has a factory on the open coast opposite the great kelp grove outside Firmin Point. This position assures a short haul of the harvested kelp, but is open to the objection of an anchorage of doubtful safety in stormy weather. The company claims that a breakwater now building will meet this objection. It is proposed to pass the wet kelp through rollers, char it, lixiviate the char, and evaporate the lixiviate in shallow pans over the charring oven. The purpose is to recover by crystallization a high-grade potassium chloride, as the raw material for the preparation of various pure potassium salts. The plans appear unnecessarily complicated and expensive for the production of potassium chloride alone. Samples of various grades of potassium chloride, charcoal, and iodine prepared by this company appear to be very satisfactory and merchantable products. The Pacific Kelp Mulch Company has offices in the Union Oil Building, Los Angeles, Cal., and a factory site at San Pedro. The site has a convenient water front, is practically beside a railroad spur, and contains a good deal of apparatus and paraphernalia used in experimental work on the production of various kelp products. This company has a cutter mounted on a decked barge, two open towing barges of 40 tons and 85 tons capacity of a special design to avoid straining in towing through a swell or heavy water, and a powerful launch. This company is reported to be building a larger and much improved cutter which will require but two men to operate; and they are building new 85-ton towing barges. Up to the present this company has been cutting and selling the wet kelp directly, last year marketing about 2500 tons. Some objections have been urged against this product, mainly as regards its price, because it has a low content of "plant foods." It is difficult, moreover, to send samples to the laboratory without loss of water en route sufficient to materially raise the content of potassium; and, finally, because it is held by some authorities that California soils are normally sufficiently supplied with potassium. Inquiries of several purchasers and users of "kelp mulch" have brought testimony favorable to the kelp. Moreover, as the accompanying table shows, the material compares quite favorably with ordinary stable manure and street sweepings, and should therefore command a commensurate price.

TABLE VI.

COMPARISON OF THE COMPOSITION OF WET KELP WITH OTHER MANURIAL PRODUCTS.

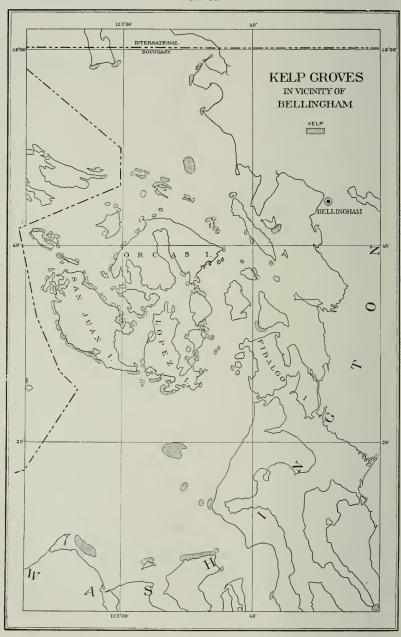
	Moisture,	Nitrogen	, Potash,	Phosphoric acid,
	Per cent.	Per cent.	Per cent.	Per cent.
Horse manure <sup>1</sup> Solid fresh excrement Fresh urine. Stable manure <sup>1</sup> . Green alfalfa <sup>1</sup> . Cowpeas <sup>1</sup> . Garbage-tankage <sup>2</sup> . Street sweepings, Washington, D. C. <sup>3</sup> Wet kelp.	73.27 75.30 78.81	0.44 1.55 .50 .72 .27 .70 .86	0.35 1.50 .60 .45 .31 .30 .55 2.50	0.17  .30 .15 .98 .60 .55

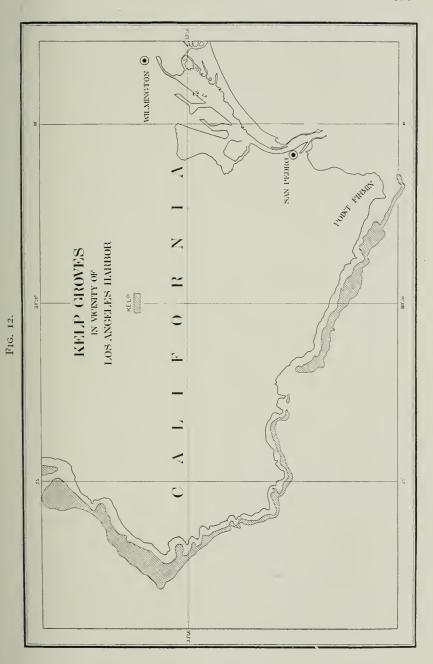
<sup>1</sup> From Soils, by S. W. Fletcher. <sup>2</sup> From Fertilizers and Crops, by L. L. Van Slyke. <sup>3</sup> From Analyses, by J. G. Smith, Bureau of Soils.

The Pacific Kelp Mulch Company is now preparing dried kelp near Ensenitas, on the Mexican coast, cutting under the Bernstein concession, and is understood to be working on a plan for artificially drying the kelp at its San Pedros plant, and expects to put the material on the market at an early date. The company is capitalized nominally at \$500,000, but has issued about two-fifths of its stock. Its promoters have invested many thousands of dollars in experimental work, an investment which appears to be in rapid recovery. The company must be recognized as the first organization to actually harvest kelp on a commercial scale, to market its product on a profitable basis, and to demonstrate, practically, that a real business opportunity exists in the production of a "kelp fertilizer."

The American Potash Company, with offices in the Los Angeles Investment Building, Los Angeles, Cal., has a most desirably located site of about 12 acres on the water front of Long Beach, Cal. This company possesses two powerful boats, as well as several smaller boats. It has absorbed the Coronado Chemical Company, formerly of San Diego, with a plant at Cardiff, and the Ocean Products Company, with a plant at Half Moon Bay, near San Francisco. The machinery and apparatus at these former plants have been moved to the Long Beach site. Experimentation on cutting kelp had been carried on by one of these companies with, it is claimed, successful results; but it is

Fig. 11.



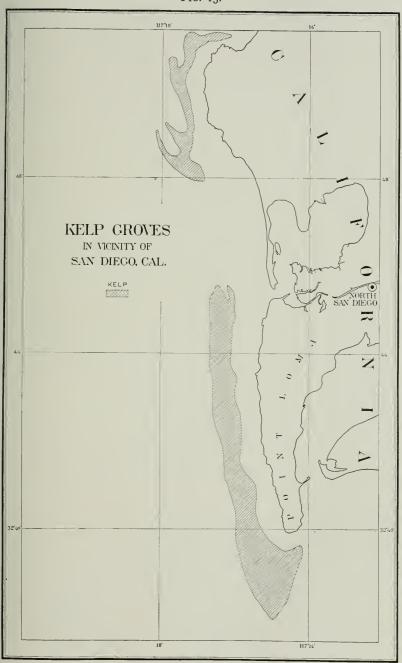


probable that this company, like all those now existing on the coast, will actually use a model more or less similar to that of the Pacific Kelp Mulch Company, illustrated in the accompanying photographs. This company announces as a result of experimentation at Half Moon Bay that it expects to produce creosote, lacquers, and various other products, potassium salts included. It is understood, however, that its main production at first will be dried kelp for fertilizer, whose profitable marketing is far better assured than the products above cited or the others described in the preliminary literature of this company. By an ingenious shaking device this company announces that it will sift the effloresced potash salts from the organic residue, thus producing a higher grade potassium chloride on the one hand, and a highly nitrogenous product on the other, the latter being susceptible of higher concentration by washing out the sodium chloride with cold water. The company has a nominal capital of \$1,500,000, appears to have sound financial backing, and to be in a position to obtain ample working capital for initial operations, securing it by a trust on the property above cited. The marketing of dried kelp and possibly other products this summer is promised.

The Pacific Products Company of Seattle, Wash., is preparing to operate on a different plan. It expects to harvest kelp on Puget Sound, where, from the nature of the plant and the weather conditions of the region, there must be a shorter season, confined to definite months. This company expects to produce oil and scrap from salmon cannery wastes. It has produced a very fine grade of oil from the livers of dog-fish, which are becoming very common in those waters, the rest of the carcasses being treated in the usual way for fish oil and scrap. Practically the same equipment will be utilized for handling fish scrap and This company has a capital stock of \$125,000. reported that 95 per cent. of the stock is owned by the directors of the company, about a fifth of the stock has been paid in for operation expenses, and that there are no bonds issued, nor outstanding indebtedness. It is also reported that the company will be prepared to market its products this summer or fall.

Desirable Locations for Manufacturing Plants.—Although there are a number of points on the Pacific coast where plants could be located for the profitable production of potash from

Fig. 13.



kelp, inspection of the working maps of the kelp groves shows four points to merit special consideration because of the proximity of abundant supplies of kelp, together with satisfactory labor and transportation facilities. These points are: Puget Sound, in the neighborhood of Bellingham or Anacortes, and Santa Barbara, Los Angeles, and San Diego, Cal.

As pointed out above, the harvest season in the Puget Sound region is short, and a kelp business will most likely command success if carried on in cooperation with the utilization of cannery wastes or other fish oil and scrap operations. general character of the kelp groves is indicated by the accompanying map (Fig. 11), showing the distribution in the neighborhood of Bellingham. The Puget Sound kelp should vield about 390,000 tons per annum of wet kelp, or enough to justify the existence in that neighborhood of 4 units of the capacity considered in the foregoing pages. As, however, the season in the Puget Sound region is probably not over half the length of the season on the southern coast, it might prove advantageous to provide 7 units, to be employed the rest of the time in handling scrap. Labor conditions in this region are fair and transportation facilities excellent. Furthermore, supplies of kelp or kelp ash from Alaska may become an added factor of importance for plants in this region.

Santa Barbara has before it a large grove of macrocystis through which a ship channel is maintained, dividing the grove into approximately equal parts. Labor conditions are probably fair and there are possible good railroad facilities. Facilities for shipment by water are not very favorable. The harbor is made practically by the kelp grove forming a natural breakwater, and the depth to landing is too shallow for large vessels and the landing facilities are meagre. The area of the Santa Barbara kelp grove is approximately 3.9 square nautical miles, and on one cutting to a depth of 4 feet would yield over 320,000 tons of wet kelp. As two cuttings a year could probably be made, over 600,000 tons should be annually available, enough to justify the existence of 6 units of the capacity described above. Other groves accessible from this point would justify an even larger installation.

From Point Firmin to Malaga Cove are two large kelp groves readily accessible from San Pedro and Long Beach, the harbors

of Los Angeles. The position and extent of these groves is indicated in the accompanying map (Fig. 12). Labor facilities are here relatively good, and both railroad and water transportation facilities are quite satisfactory. One of these groves has an area of about 0.76 square nautical mile and is estimated to be able to produce on one cutting to a depth of 4 feet about 62,500 tons of wet kelp, or 125,000 tons on two cuttings. The large grove contains about 1.6 square nautical miles and should vield 131,500 tons of wet kelp on one cutting, or over 260,000 tons on two cuttings. 'Other accessible groves in the neighborhood augment considerably this estimated production. There is enough kelp in this neighborhood to justify the installation of 4 units of the capacity discussed above. The three companies already installed in this neighborhood should, before long, practically monopolize the kelp production in the immediate vicinity. Outside the harbor of San Diego, between Point Loma and La Iolla, as indicated on the accompanying map (Fig. 13), lie two large groves of very heavy kelp. The combined area of these two groves is about 7.7 square nautical miles, and it is estimated that they should produce 633,000 tons of wet kelp on one cutting to a depth of 4 feet, or 1,265,000 tons on two cuttings. This tonnage alone would justify 12 or 13 units, but, considering the position of San Diego with respect to the numerous large groves on the Mexican coast, 15, or even perhaps 20, units could be surely supplied with raw material. Labor facilities at San Diego are fair, railroad facilities are good and improving, and facilities for transportation by water excellent. Plant sites which are now cheap are likely, however, to be much more costly in the near future. All things considered, San Diego appears to offer unusual advantages for a large and profitable production of "potash from kelp."

Purification and Concentration of Radium Barium Chlorides. E. Ebler and W. Bender. (Ber., xlvi, 1571.)—When hydrochloric acid gas is led into mixtures of barium and radium chlorides till it produces precipitation, the first fractions precipitated are richer in radium than the later ones, and practically the whole of the radium is precipitated before 75 per cent. of the barium is. This method of enrichment is far preferable to that of fractional precipitation as sulphate from every point of view.

"Bungo" Sulphur. Anon. (Oil, Paint and Drug Rep., May 12, 1913.)—In Bungo province, Japan, there are many geyser-like craters which emit sulphurous fumes intermittently when volcanic activity induces action. During their inactive periods the Japanese have placed pipes in the ground and in the crevices about the craters of these so-called geysers in such a position that when the active period commences the fumes are collected in these pipes and conducted into hermetically tight reservoirs, from which the condensed sulphur flows down the mountain side in long, light conduits, where it solidifies, and from which it is taken, broken into irregular pieces, sacked and transported by coolies to the markets and sold under the name of Bungo sulphur.

Solubility of Sulphur in Rubber. H. LOEWEN. (Gummi Zeit., xvii, 1301.)—The following experimental evidence supports the view that one of the phenomena of vulcanization consists of the solution of sulphur in the rubber. A small quantity of a mixture of Para rubber with 10 per cent. of sulphur was pressed between a microscope slide and a cover-glass, warmed to about 80° C., and heated in a hot-air oven at 130°-140° C. The slide was examined at intervals under the microscope. After a very short heating the sulphur was found to be distributed through the mass in globules of various sizes; when the heating had continued for 20 to 30 minutes, the mass appeared perfectly clear and transparent immediately after removal from the oven, but on cooling became cloudy to the naked eye. This turbidity is due to the separation of small globules of super-cooled liquid sulphur, which crystallize on standing. That this is a case of ordinary molecular solution, and not of colloidal solution, is shown by several experimental results, two of which are quoted: (1) If the slide be heated for increasing length of time until the point is reached when the preparation just remains clear on first cooling down, the free sulphur separates from the cooled mass in the crystalline form, and not in liquid drops which crystallize afterwards. The solubility of sulphur is higher in vulcanized than in unvulcanized rubber, and this agrees with the fact that highly vulcanized rubber, ebonite, does not "sulphur up," although containing high percentages of free sulphur. (2) If a fragment of rubber without sulphur be pressed between slide and cover-glass, and molten sulphur be applied round the edges of the glass so as to be drawn into contact with the rubber by capillary action, and the preparation be then heated in the oven for about 45 minutes, the sulphur diffuses into the rubber for a considerable distance in a manner characteristic of true solution. In view of these results it is considered that adsorption plays no part in the process of vulcanization, the three stages of which are fusion of the sulphur, solution of the sulphur in the rubber, and the chemical combination of sulphur with rubber.

# THE USE OF THE SYNCHRONOUS COMMUTATOR IN ALTERNATING CURRENT MEASUREMENTS.\*

BY

## FREDERICK BEDELL, Ph.D.,

Professor of Applied Electricity in Cornell University.

Although the commutator or rectifier has been used in a number of laboratories for making certain alternating current measurements, and although some of its uses for specific purposes have been described or referred to by various writers whose names are given later, the uses to which it can be put do not seem to be widely known, nor has there been any general discussion of the subject. So wide is its scope—giving a direct method for measuring alternating flux, for measuring maximum voltage in insulation and other testing, superseding, in a way, the older methods of instantaneous contact for determining alternating current wave form, and making available direct current galvanometers and other instruments for various kinds of alternating current measurements—that it is believed a better knowledge of the possibilities of the rectifying or integrating commutator will lead to its more common use in our testing and educational laboratories.

The underlying principles of the methods here described are not new; some features in their development and application, however, are now described for the first time.

The mechanical structure of the apparatus may be varied; any form of switch can be used that reverses the circuit connections twice each cycle. A simple arrangement of apparatus for accomplishing this is as follows:

A commutator is driven in synchronism with the alternating current upon which tests are to be made, being direct-connected to a small synchronous motor or mounted on the shaft of the supply generator. The commutator has as many segments as the machine upon which it is mounted has poles. Alternate segments are connected together, thus forming two sets of segments that are connected, respectively, to two slip rings upon

<sup>\*</sup> Communicated by the author.

which bear two brushes, b b', which can be connected to a source of alternating current to be measured. Bearing upon the commutator, and accurately set so as to be separated from each other by a distance of one commutator segment, are two brushes B B' from which can be derived rectified current that can be read by a direct current measuring instrument. These brushes are so mounted that, without changing the distance between them, they can be shifted and their position read upon a scale graduated in degrees. When the brushes are given such a position that commutation takes place at the zero point of the alternating current wave, the alternating current becomes completely rectified so as to be unidirectional.

It will be noted that each degree of mechanical shifting of the brushes corresponds to one degree of electrical phase when the driving machine has two poles, to two degrees of electrical phase when the driving machine has four poles, and so on. A tangent screw or some fine adjustment for setting the brushes should be provided. It is desirable that means be provided for conveniently shifting the brushes by successive equal steps of say 5 degrees or 10 degrees, and also for shifting them quickly through 90 degrees of electrical phase. A form of apparatus used by the writer is shown in Fig. 1.

It will be seen that any commutator of this general type can be used only on alternating currents that change sign every half cycle and have similar positive and negative waves; it can be used on all usual alternating current circuits, but not in the unusual case in which even\* harmonics are present. This limitation does not apply to the condenser discharge method for the determination of wave form of voltage and current (Part VII), for this method can be applied to any pulsating wave, unidirectional as well as alternating, that varies periodically; that is, there may be present even as well as odd harmonics and also a constant term.

Thin metallic brushes should be used, that can be set accurately without bridging across adjacent commutator segments; the resistance of brushes and contacts should be as low and

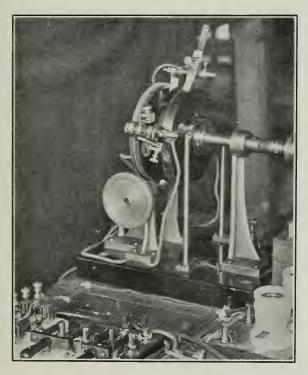
<sup>\*</sup> When both odd and even harmonics are present, methods IV, V, and VI can be used to determine the wave form of the sum of the odd harmonics only. The wave form of the sum of the even harmonics can be determined by a separate commutator with twice as many segments.

uniform as possible, for in some of the methods these conditions contribute to the precision of the results. The commutator and galvanometer circuit should be well insulated from the motor and its circuits, particularly from the direct current field circuit.

The following uses of the commutator will be discussed:

- I. Determination of average value of alternating electromotive force and current.
  - II. Use as zero instrument.

Fig. 1.



- III. Determination of form factor of alternating current or voltage.
- IV. Determination of wave form and maximum value of alternating magnetic flux.

The determination of wave forms and maximum values of alternating currents and electromotive forces:

V. By the air transformer method.

VI. By the condenser current method.

VII. By the condenser discharge method.

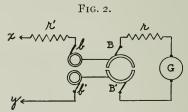
VIII. The determination of phase difference.

IX. General and historical.

In preparing this paper it has been the writer's aim to describe the essential elements of the several methods. Modifications may be made in arrangement of apparatus, in procedure, and in methods of calibration to suit the requirements of particular cases.

# I. DETERMINATION OF AVERAGE VALUE OF ALTERNATING ELECTROMOTIVE FORCE OR CURRENT.

Electromotive Force.—To determine the average value of the alternating electromotive force between the line terminals xy, the line is connected through the rectifying commu-



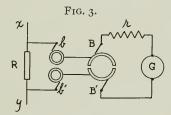
Arrangement of commutator and galvanometer.

tator to a D'Arsonval galvanometer G,—which in this case may be a Weston direct current voltmeter,—as shown in Fig. 2. One pair of brushes is connected to the line; the other pair to the galvanometer. A non-inductive resistance or multiplier r is connected in series on the galvanometer side of the commutator; when a voltmeter is used this resistance may be contained as part of the instrument. In comparison with r, the resistance of the brush contact and the inductance of the galvanometer will usually be insignificant. When the line voltage is higher than can be commutated without danger of sparking or short-circuiting,—that is, in practically all voltage measurements,—additional series resistance r' should be placed on the line side of the commutator, or the line voltage should be stepped down by a transformer. The procedure to be followed in taking readings is described below.

To obtain the actual voltage across xy, when resistances r

and r' are used, the readings of the galvanometer or voltmeter should be multiplied by a proper constant; or the instrument should be calibrated on direct current \* with these resistances in circuit by comparison with a standard direct current voltmeter.

Current.—To determine the average value of an alternating current, insert in series with the circuit a low non-inductive resistance R (commonly called a shunt) and connect the terminals of R through the commutator to the galvanometer G, which may be a millivoltmeter, as shown in Fig. 3. Connections should be well made so that the resistance remains as constant as possible. A resistance r in the galvanometer circuit will reduce any error due to inductance of the galvanometer or to variable resistance of brush contact, but for the same sensi-



Connection for current measurement.

tiveness will require a correspondingly greater resistance and voltage drop in R, which may be a disadvantage.

The resistance r is better placed on the galvanometer side rather than the line side of the commutator in this case (and in similar low potential cases, as, for example, the air transformer method for determining current), so that any static electricity that might be generated in the commutator would flow through R rather than through G,—an effect usually negligible, however.

The instrument may be calibrated on direct current by comparing its reading with a standard ammeter connected in series

<sup>\*</sup> If the commutator is running during the calibration on direct current, G will not read unless placed on the line side of the commutator in series with r'. If a suppressor (described later) is used instead of a commutator, the suppressor may be running and G will read on direct as well as on alternating current without this transfer. The use of a suppressor has this advantage.

Calibration can be made upon an alternating current circuit of known form factor f, the average voltage being equal to the effective voltage measured by a standard alternating current voltmeter divided by f.

with the line. If the commutator is running (as it should be when the highest accuracy is desired), G must be transferred to the other side of the commutator, being in series with the connection between R and the commutator (see preceding note).

For measuring very small currents, the shunt R can be omitted, so that all the current is commutated and passes through the galvanometer.

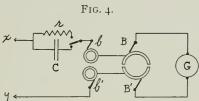
Procedure.—In measuring alternating current or voltage by this method, commutation should take place at the zero point of the alternating wave. The deflection of G will then be a maximum and will accurately indicate the average value of current or voltage. There are several methods by which the proper reading can be obtained.

- (I) Maximum Deflection Method.—The brushes are shifted until the deflection of G is a maximum, when a reading is taken. This method is correct in principle, but it is not easy to quickly set for a maximum.
- (1a) Maximum Deflection Method with Non-Synchronous Commutator.—If the commutator is driven slightly off from synchronism, as through a series of gears by a synchronous motor or directly by an induction motor, no shifting of the brushes is necessary. The deflection of G has beats; a reading is taken when the deflection is a maximum. This method is correct in principle; readings cannot be taken with great accuracy.
- (2) Special Contactor Method.—A second galvanometer, G, in an independent auxiliary circuit, is connected in circuit at a definite instant in each revolution by a revolving contact-making point P touching an adjustable brush B'', as in the well-known instantaneous contact methods. P is in line with the insulation between commutator segments; B'' is in line with one of the brushes BB' and is carried by the same rocker arm.

The brushes are shifted until G' reads zero, thus insuring commutation at the zero point of the alternating wave; a reading of G is then taken. A condenser in parallel with the second galvanometer G' will increase its sensitiveness.

This method is correct in principle and gives rapid and accurate readings. It requires, however, a special contactor as described. A single galvanometer with suitable switches can be used, but the method is far more convenient with two instruments.

(3) Condenser Method for Commutating at Zero.—The resistance r is placed on the line side of the commutator as in Fig. 4. The resistance of the galvanometer circuit should be small. A switch is arranged so that a condenser C may be connected in circuit in place of the resistance r. With C in circuit, the brushes are moved until G reads zero, thus locating the zero of the wave as in the condenser current method (Part VI) discussed later; the resistance r is then substituted for C and a reading of G is taken.



Condenser method for commutating at zero.

This method insures correct commutation at zero for all wave forms, requires no special apparatus—other than a condenser—and is simple in operation.

(4) Quadrature Shift of Brushes.—The brushes are moved until G reads zero, and are then shifted 90 degrees of phase, or one-quarter cycle; readings of G are taken.

This method is positive in taking readings, but may introduce error with irregular shaped waves, for commutation is not necessarily at the zero point, as it should be, being 90 degrees from a median line dividing the wave area in half. Shifting the brushes 90 degrees may be a tedious process, unless the apparatus is specially constructed with this in view.

(5) Quadrature Shift of Synchronous Motor.—The quadrature shift may be made not by shifting the brushes but by throwing the synchronous driving motor from one phase to the other of a two-phase supply circuit. This introduces the same error as is introduced by shifting the brushes, and may introduce additional error if the two phases of the supply circuit are not in exact quadrature.

Uses.—The commutator method for measuring alternating currents makes possible the accurate measurement of very small alternating quantities—milliamperes, millivolts, and smaller—which cannot be measured by the usual instruments or methods.

The average value of an alternating current or electromotive force gives data for determining form factor, discussed in a following section.

As the average value obtained by the commutator method is the algebraic average for a half cycle, the average value and form factor thus obtained lose significance when applied to any voltage or current that is not continuously of one sign for half a cycle. (This limitation does not apply to any of the methods for determining wave form described in the subsequent sections.)

## II. USE AS ZERO INSTRUMENT.

By means of the rectifying commutator, arranged as described in Part I, any D'Arsonval galvanometer or other direct current instrument can be used as a zero instrument on alternating current with the same sensitiveness as on direct current. It thus becomes a most satisfactory instrument for potentiometer measurement or bridge measurement on alternating current circuits. With the synchronous commutator, the brushes are first set for a maximum galvanometer reading; circuit conditions are then changed until the galvanometer reads zero or a minimum. With a non-synchronous commutator the shifting of the brushes becomes unnecessary.

In balancing a known and an unknown quantity in potentiometer measurement so as to obtain a zero reading it should be kept in mind that the commutator method balances the average values of the two quantities, whereas a dynamometer balances effective values and a vibration galvanometer balances the values of the fundamental or other harmonic to which it is tuned. In some cases these differences may become significant. (The above statement in regard to the dynamometer refers to its use in the usual manner, and not to its use with separate excitation, in which case the wave form of the excitation should also be considered.)

## III. DETERMINATION OF FORM FACTOR OF ALTERNATING CURRENT OR VOLTAGE.

The form factor, f, of an alternating current or voltage is found by dividing its effective value by its average value.

The effective value may be found by a dynamometer or A.C. instrument D, connected across the line. The average value may

be found, as in Part I, by a commutator and galvanometer or D.C. instrument G, which is read when a maximum and has previously been calibrated in terms of D.

As D will read on D.C. as well as on A.C., a simpler procedure is to connect D on the same side of the commutator as G, the two instruments being in parallel. Any resistances r' or r in series with the two instruments, as in Fig. 2, may be of unknown value. Simultaneous readings, d and g, of the two instruments are first taken on alternating current with the commutator running, the brushes being set so that g is a maximum. Readings d' and g' are then taken on direct current with the commutator stationary. No further calibration is necessary. The form factor is then f = d  $g' \div d'$  g. For greatest accuracy the readings on direct and on alternating current should be on about the same parts of the scales.

Form factor may be found by first determining the instantaneous values of the wave by one of the methods subsequently described. The effective value is the square root of the average of the squares of equidistant instantaneous values for one-half cycle. Or, if the instantaneous values are plotted as a polar curve, the effective value is the square root of  $2/\pi$  times the area of the polar curve for half a cycle, as found by a planimeter. The average value may be found by averaging the instantaneous value; or it may be found from the area of the curve plotted with rectangular coördinates.

As an illustration of the significance of form factor, the maximum value of the flux in a transformer (upon which depend the core losses) is directly proportional to the average value of the voltage, which in turn is equal to the effective measured voltage divided by the form factor.

# IV. DETERMINATION OF WAVE FORM AND MAXIMUM VALUE OF ALTERNATING MAGNETIC FLUX.

Wave Form of Flux.—From the terminals xy of a coil (preferably a secondary coil) embracing the flux to be measured, connections are made through the synchronous commutator and suitable resistances, as in Fig. 2, to the galvanometer G, which in this case may advantageously be a Weston voltmeter. Let V be the reading of the galvanometer or voltmeter calibrated, with the commutator running, to read volts at

the terminals xy. Let S be the number of turns in the coil, and let n be the frequency of the circuit.

If readings of V are taken for successive positions of the commutator brushes, the instantaneous value of the flux corresponding to any reading is

$$\varphi = \frac{V \times 10^8}{4nS} \cdot$$

The wave form of flux is thus determined.

The only other method for obtaining a wave form of flux is to derive it by integration from the wave form of voltage, and this may be done as a check. The usual procedure \* is to integrate by means of a planimeter, which is somewhat laborious.

Maximum Flux.—The maximum value of flux is determined by the maximum reading of V, which is the average voltage, or  $E_{av}$ ; that is,

$$\varphi_{max.} = \frac{V_{max.} \times 10^8}{4nS} = \frac{E_{av.} \times 10^8}{4nS}.$$

It is seen that the maximum flux in a magnetic circuit, as for example in a transformer, depends upon the average value of the voltage, rather than upon the maximum or effective value. When only maximum values of flux are desired, a non-synchronous commutator can be used; or any of the procedures can be followed that were described in Part I for determining average voltages.

*Proof.*—These relations may be proved as follows: We have the fundamental relation  $d\varphi = -e dt \div S$ . During any time interval of half a period T,—that is, from any time  $t = t_1$  to  $t = t_1 + \frac{T}{2}$ ,—the flux changes from  $+\varphi$  to  $-\varphi$ , the negative and positive waves being similar. Integrating, therefore, for half of a period, we have

$$\int_{+\phi}^{-\phi} d\varphi = -\frac{\mathrm{I}}{S} \int_{t_1}^{t_1 + \frac{T}{2}} e \, dt.$$

<sup>\*</sup>A simpler procedure than integrating by a planimeter is as follows: Let  $y_1, y_2, y_3, \ldots, y_n$ , be successive equidistant ordinates of the electromotive force wave, beginning arbitrarily with any initial ordinate  $y_1$ ; these ordinates may or may not be actually plotted. The corresponding ordinates for the flux wave are proportional to  $y_1, (y_1 + y_2), (y_1 + y_2 + y_3), \ldots, (y_1 + y_2 + \ldots, y_n)$ , in each case being proportional to the algebraic sum of any particular ordinate  $y_n$  and all preceding ordinates.

But the reading of the voltmeter is

$$V = \frac{2}{T} \int_{t_1}^{t_1 + \frac{T}{2}} e \, dt,$$

this being the average ordinate of the voltage curve during a half cycle subsequent to any time  $t_1$ . Hence we may write

$$-2 \varphi = -\frac{TV}{2S}.$$

Substituting I/n for T, and introducing  $IO^8$  when V is in volts, we have

$$\varphi = \frac{V \times 10^8}{4nS} ,$$

which is the value of the flux at the time  $t_1$  and (with change of sign) at the time  $t_1 + \frac{T}{2}$ . The reading of the voltmeter depends solely upon the value of the flux at the time of commutation, and is independent of any intermediate values.

V. AIR TRANSFORMER METHOD FOR THE DETERMINATION OF WAVE FORM AND MAXIMUM VALUE OF ALTERNATING CURRENT AND ELECTROMOTIVE FORCE.

Wave Form of Current.—The primary of an air core transformer is connected in series in the circuit in which the instantaneous value of the current  $i_1$  is to be determined. The secondary of the transformer is connected, through the synchronous commutator, to the galvanometer or voltmeter. The resistance of the secondary and galvanometer circuit should be high, so that the effect of self-inductance in this circuit is small. Letting M be the mutual inductance of the transformer, we have the secondary voltage

$$e_2=Ri_2=Mrac{di_1}{dt}$$
, or  $di_1=e_2dt\div M$ .

Hence, by a proof similar to that previously given (Part IV), the instantaneous value of the current corresponding to any reading V (in volts) of the galvanometer or voltmeter is

$$i_1 = \frac{V}{4nM},$$

where n is the frequency of the circuit.

As the commutator brushes are shifted into successive positions, the reading V multiplied by a proper constant will thus give the instantaneous value of current.

When M is not known, the proper constant can be found by comparing the effective value of the current, as measured by a standard ammeter, with the effective value found by taking the square root of the mean square of the instantaneous values, or by taking the square root of  $2/\pi$  times the area of a curve plotted in polar coördinates, for half a cycle. Other methods of calibration may suggest themselves.

By varying the relative positions of the primary and secondary windings, the value of M and so the sensibility of the galvanometer can be varied at will.

In determining the wave form of current of a high potential circuit this method has the advantage that the air transformer

insulates the testing apparatus from the line circuit.

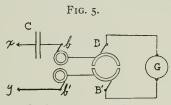
Wave Form of Electromotive Force.—The primary of the air transformer, in series with a high resistance  $R_1$ , is connected across the circuit under test. The commutator and galvanometer or voltmeter are connected to the secondary as before. The fall in potential due to  $R_1$  must be large compared with the inductive electromotive force in the transformer primary, so that the primary current at any instant will be proportional to the line voltage at that instant. The proper constant can be found by calculation or by calibration as described above. If the maximum voltage of some circuit is known, this value may be compared with the maximum reading of the galvanometer.

The air transformer method gives more difficulty in calibration than the condenser current or condenser discharge method described later, and is subject to error if the circuit constants are not suitably chosen. It seems to have a wider range of usefulness in determining wave form of current than of voltage. For very high voltages it is not so well suited as the condenser current method; nor is it so well suited for very low voltages on account of the necessarily high resistance  $R_1$ .

Maximum Values.—The maximum value of the current or the voltage is determined by the maximum reading of the instrument as the brush position is varied. When maximum values only are desired, a non-synchronous commutator can be employed or various procedures can be followed as given in Part I.

VI. CONDENSER CURRENT METHOD FOR THE DETERMINATION OF
WAVE FORM AND MAXIMUM VALUE OF ALTERNATING
CURRENT AND ELECTROMOTIVE FORCE.

Wave Form of Electromotive Force.—A condenser C is connected across the line, xy, the voltage of which is to be determined. The condenser current is commutated and is measured by a suitable milliammeter, millivoltmeter, or low-resistance galvanometer, G, as shown in Fig. 5. The sensitiveness of the arrangement can be varied by changing the value of the capacity, C, or by means of a resistance in shunt with the galvanometer on either the galvanometer side or line side of the commutator.



Condenser current method.

G is calibrated so as to give current in ampères. Let A be the current reading of the instrument thus calibrated, and let n be the frequency of the circuit.

If readings A are taken for successive positions of the commutator brushes, the instantaneous value of the line voltage corresponding to any reading is

$$e = \frac{A}{4nC}.$$

This determines the wave form of voltage.

For accuracy the resistance r of the galvanometer circuit, including the commutator, should be small compared with the reactance x of the condenser. There is little difficulty in selecting an instrument and a capacity so that this condition will hold. Where a number of current and voltage curves are to be taken and their phase positions are to be accurately determined, for greatest accuracy r/x should have the same value in taking each curve,—i.e., when x is changed r should be changed to correspond, but in most cases this refinement is unnecessary. Thus, taking a case in which r=2.75 ohms, C=0.4 m.f., and n=60,

we have x = 6640 and r/x = 0.0004. The phase shifting of the condenser current due to r is  $tan^{-1} r/x$ , a little over one minute. The impedance ( $\sqrt{r^2 + x^2} = 6640.00057$ ) is practically determined by x alone, the resistance having negligible effect on the impedance and on the amplitude of the current.

In range and in sensitiveness the condenser current method surpasses all other methods. The voltage may be a fraction of a volt or the highest voltage obtainable; with suitable shunts a

current of practically any magnitude can be measured.

Wave Form of Current.—To determine the wave form of current, a resistance, or so-called shunt, R, is connected in series with the line. The condenser C is connected across its terminals, the commutated condenser current being measured by the galvanometer G. The wave form of current is thus determined in the same manner as the wave form of voltage.

Maximum Values.—The maximum value of current or voltage is determined by the maximum reading of the instrument, that is, by the average value of the condenser current,—and, as already mentioned, a non-synchronous commutator may be used in this determination. The condenser current method may well be used for testing the maximum values of very high voltages, as in insulator testing.

Proof.—The relation at any instant between the charge q of the condenser and the current i is dq = i dt. During any time interval of half a period T,—that is, from any time  $t = t_1$ to  $t = t_1 + \frac{T}{2}$ —the charge changes from +q to -q, the positive and negative waves being similar. Integrating for half a period, we have

$$\int_{+q}^{-q} dq = \int_{l_1}^{l_1 + \frac{T}{2}} i \, dt \, .$$

But the reading of the galvanometer or millivoltmeter, calibrated to read ampères in R as described above, is

$$A = \frac{2}{T} \int_{t_1}^{t_1 + \frac{T}{2}} i \, dt \,,$$

this being the average value of the current during a half cycle subsequent to any time  $t_1$ . Hence we may write

$$2q = \frac{TA}{2}$$
; or,  $q = \frac{TA}{4}$ .

Writing I/n for T, and Ce for q, we have

$$e = \frac{A}{4nC} \cdot$$

The equation for e depends upon e being constant, which is true for an air condenser and practically true for a mica condenser. For a condenser with an inferior dielectric this relation is not true, and for such a condenser the method is correct for determining the instantaneous values of e but not of e. If the instantaneous values of e were accurately determined by some other method, data would be thus obtained for plotting a possible dielectric hysteresis loop \* between e and e.

VII. CONDENSER DISCHARGE METHOD FOR THE DETERMINATION
OF WAVE FORM AND MAXIMUM VALUE OF ANY PERIODICALLY VARYING ELECTROMOTIVE FORCE

OR CURRENT.

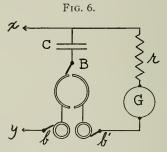
Wave Form of Electromotive Force.—For determining the instantaneous values of any periodic electromotive force or current by the method of condenser discharge, the commutator is used not as a rectifier but as a synchronous switch for charging a condenser and discharging it through a galvanometer at a definite time in each cycle. A mica condenser should be used, or one in which the absorption is negligible. The arrangement of circuits is shown in Fig. 6. Bearing on the slip rings are the two brushes b b'; bearing on the commutator is the single brush B. (Any idle brush should be removed.) As the commutator is driven synchronously, it will be seen that the condenser is charged from the line until a definite instant in each cycle, depending upon the position of the brush B, and is then discharged through the galvanometer G. The reading of G depends upon the charge of the condenser, and hence upon the line voltage, at the last instant of charging. By setting B successively in dif-

<sup>\*</sup>Such a loop is given by Bedell, Ballantyne and Williamson, Phys. Rev., vol. i, p. 81, 1893; Trans. A. I. E. E., vol. x, p. 525, 1893; also Nichols' "Laboratory Manual," vol. ii, p. 193.

ferent positions and taking corresponding readings of G, the complete wave form can be determined.

The instrument G should be well damped. In determining wave form of voltage, a Weston voltmeter may be used, or a millivoltmeter with resistance r in series. To allow time for the condenser to discharge, it is desirable (although not necessary) to have the time-constant—resistance times capacity—of the discharge circuit less than one-half period. No resistance should be placed on the line side of the condenser or commutator. Calibration for voltage or current is made with direct current with the commutator running at proper speed.

The condenser discharge method will be found generally convenient through a moderate range on account of its easy calibra-



Synchronous switch and condenser discharge method.

tion and its applicability to any periodic current or voltage, there being no limitation to symmetrical alternating current waves. It cannot be used directly on a very high voltage circuit, as can the condenser current method. On such a circuit a high resistance should be bridged across the line, the apparatus shown in Fig. 6 being tapped off of part of it. On an alternating current line a transformer or auto-transformer can be thus used.

The alternate sets of commutator segments need not be of equal length in the condenser discharge method, as required in all the preceding methods; nor need the number of segments be identical with the number of poles. Thus, a commutator with two segments driven by a four-pole synchronous motor would charge the condenser for two half cycles and discharge it for two half cycles, if the segments were equal. This flexibility in equipment may at times prove a convenience.

Wave Form of Current.—For determining the wave form of

current a non-inductive resistance is placed in series with the circuit under test, the apparatus as shown in Fig. 6 being connected to the terminals of this resistance. In current measurements a galvanometer or millivoltmeter may be used; the resistance r should be small or omitted entirely.

Maximum Values.—Maximum values are determined by the maximum readings, as already discussed in Parts V and VI.

#### VIII. DETERMINATION OF PHASE DIFFERENCE.

The difference in phase between two alternating waves may be determined by ascertaining the difference in phase between their zero points. Using the same method of measurement on the two waves (as the air transformer method, condenser current method, or condenser discharge method) and so far as possible the identical circuits and apparatus,\* a zero setting is found first for one wave, then for the other, and their difference determined. This does not necessitate calibration nor the determination of the complete wave forms unless these should be desired in those cases in which the two wave forms are very different. In such cases, however, phase difference has no exact significance, except by special definition. Instead of setting for zero, it is sometimes convenient to take a reading on each side of zero and to locate the zero by a plot or by interpolation.

Another method, sometimes adequate, is to make use of the methods of measurements described in Part I for the determination of average value of current or voltage. With the apparatus thus set up, zero settings are made first on one circuit and then on the other and the phase difference determined. The phase difference between two quantities thus determined means the phase difference between their median lines—lines dividing their wave areas in half. If the two waves have the same shape, the phase difference between their median lines will be the same as the phase difference between their zeros; if they do not have the same shape, the significance of phase difference is questionable, as already pointed out.

<sup>\*</sup>When changes are made, they should be so made as to obtain relative accuracy in phase; thus, in the condenser current method, for example, any change in reactance should be accompanied by a compensating proportional change in resistance.

Vol. CLXXVI, No. 1054-29

Other methods may be employed that are beyond the scope of the present paper. The methods here briefly described are incapable of any such accuracy as that attained, for example, in the several special methods for determining phase difference in instrument transformers now in use in some of our testing laboratories; but, while they are not precision methods, they are adequate for certain general purposes.

#### IX. GENERAL AND HISTORICAL.

The object of this paper has not been to give the results of investigations made by means of the synchronous commutator. nor to give a detailed description of a particular form of apparatus, but rather to give a statement of the various methods of its use. Several forms of apparatus will be found described in the references given below. The commutator, as described in this paper, makes use of the complete alternating current wave by reversing the circuit connections every half wave. A simpler form of apparatus suppresses alternate half waves instead of reversing them. Such an apparatus, which may well be termed a suppressor, will be found described in several of the references given. For a two-pole machine, a suppressor may consist of two brushes, side by side, resting upon a cylinder mounted upon the shaft of the machine. One-half the cylinder (180°) is conducting, the other half being non-conducting, so that the circuit between the two brushes will be closed during alternate half cycles. A suppressor may be placed in series or in shunt with a galvanometer, thus suppressing alternate half waves either by opening the galvanometer circuit or by short-circuiting it. With a suppressor the galvanometer becomes less sensitive than with a rectifying commutator; furthermore, a suppressor cannot be used for the condenser discharge method, nor can a series suppressor be used with the condenser current method. On the other hand, with a suppressor, calibration in some cases is. simpler and short-circuiting, that may give trouble with a commutator, becomes impossible. The commutator described in this paper may be used as a suppressor by using two brushes, b B, only, the other brushes being removed.

The method for determining the wave form of flux and the air transformer method for determining the wave form of cur-

rent and voltage are mentioned by Sahulka 1 (who illustrates diagrammatically a non-synchronous suppressor that with a four-pole machine suppresses seven half waves and retains one) and are fully developed and described by Townsend,2 who gives experimental results and a discussion of the theory of the methods. A synchronous commutator for the same purpose is described by Lyle 3 and by Lloyd and Fisher.7 Townsend mentions the possibility of determining curves of quantity; this and the question of a hysteresis loop for a condenser is taken up in the discussion of his paper. Sumpner 5 has made use of a suppressor and galvanometer for measuring the average value of very small alternating currents, not otherwise measurable, and for determining form factor. Hospitalier 4 made use of a non-synchronous commutator with unequal segments for condenser discharge in operating his ondograph, and later Robinson 6 made similar use of a synchronous commutator, also with unequal segments, in operating the wave-meter of the General Electric Company. Robinson,8 and Sharp and Crawford,9 describe forms of synchronous commutators and the use of a direct current galvanometer as a zero instrument in alternating current testing. Sharp and Crawford employ not the usual revolving commutator but a reversing switch operated by a revolving cam. Chubb and Fortescue 11 have recently made use of a synchronous and also a non-synchronous suppressor in parallel with a galvanometer and in series with a condenser for measuring maximum voltages of very high value, but they make no mention of the determination of wave form. Measurements were made by them up to several hundred thousand volts by using an air condenser, one member of which was fifteen feet in length. The measuring apparatus was grounded and protected by shields, also grounded. Bedell <sup>12</sup> describes the condenser current method for determining wave form as here given. Morrison 10 describes a more elaborate form of commutator for integrating waves in which even harmonics are present.

The underlying principle developed in these methods is as follows:

To obtain the wave form of a quantity, this quantity is first differentiated with respect to time (by some inductive or other device) and is then integrated by a galvanometer, the desired limits of the integral being assigned by the commutator. The

procedure may be extended to other quantities than those described.

For determining wave form of current and voltage, the commutator methods here described—employing a contact of definite duration—are superior in reliability and in sensitiveness of instrument reading to the well-known methods of instantaneous contact employing a contact of infinitely short duration. Some quantities, as flux, readily determined by the commutator can at present be directly determined by no other method.

#### REFERENCES.

- <sup>1</sup> J. Sahulka, "Contact-Vorrichtung für Wechselstrom-Dynamos," Zeit. für Elektrotechnik, vol. xvi, p. 4, Jan., 1898.
- <sup>3</sup> F. Townsend, "A New Method of Tracing Alternating Current Curves," Trans. A. I. E. E., vol. xvii, p. 5, Jan., 1900.
- <sup>3</sup> T. R. Lyle, "Preliminary Account of a Wave Tracer and Analyzer," *Phil. Mag.*, vol. 6 (6th Series), p. 549, Nov., 1903.
- \*E. Hospitalier, "The Slow Registration of Rapid Phenomena by Strobographic Methods," Jour. Brit. Inst. of E. E., vol. 33, p. 80, Dec., 1903.
- W. E. Sumpner, "The Measurement of Small Differences of Phase," *Phil. Mag.*, p. 155, Jan., 1905.
- <sup>1</sup>L. T. Robinson, "The Oscillograph and its Uses," Trans. A. I. E. E., vol. xxiv, p. 195, Apr., 1905.
- <sup>†</sup> M. G. Lloyd and J. V. S. Fisher, "An Apparatus for Determining the Form of a Wave of Magnetic Flux," Bul. Bureau of Standards, vol. 4, p. 467, May, 1908.
- L. T. Robinson, "Electrical Measurements on Circuits Requiring Current and Potential Transformers," Trans. A. I. E. E., vol. xxviii, p. 1024, June, 1909.
- <sup>o</sup> C. H. Sharp and W. W. Crawford, "Some Recent Developments in Exact Alternating Current Measurements," *Trans. A. I. E. E.*, vol. xxix, p. 1517, July, 1910.
- "M. Morrison, "Mechanical Integration of the Electromotive Force when Even Harmonics are Present," Southern Electrician, p. 60, August, 1911; see also p. 238, June, 1911.
- <sup>11</sup> L. W. Chubb and C. Fortescue, "Calibration of the Sphere Gap Voltmeter," A. I. E. E., Feb. 28, 1913.
- <sup>12</sup> F. Bedell, "Condenser Current Method for the Determination of Alternating Wave Form," *The Electrical World*, vol. lxii, August 23, 1913.

## BIOCHEMICAL STUDIES OF CHOLESTEROL.\*

BY

JOSEPH SAMUEL HEPBURN, A.M.; B.S. in Chem.; M.S.; University Fellow in Biological Chemistry.

## I. INTRODUCTION.

#### ORGANIC CHEMISTRY OF CHOLESTEROL.

CHOLESTEROL belongs to the class of lipins,† and is widely distributed throughout the animal world. Chevreul,¹ the Father of the Chemistry of the Fats, prepared pure cholesterol from human biliary calculi, and attempted to saponify it by prolonged heating with a solution of potash in a mixture of alcohol and water, but without success. From this experiment doubtless arose the term "unsaponifiable fat" which is occasionally applied to cholesterol and certain closely-related compounds.

Berthelot <sup>2</sup> recognized cholesterol as a monatomic alcohol, and prepared certain of its esters; he suggested that cholesterol

The aliphatic lipins are subdivided into simple and conjugate lipins. The simple lipins include the natural fats, fatty oils, waxes, fatty acids, soaps and higher monohydric aliphatic alcohols. The conjugate lipins include proteolipins such as ovovitellin, glycolipins such as cerebrogalactosides, phospholipins such as lecithin, and glycophospholipins such as carnaubon.

The *carbocyclic lipins* include the *sterols* (cholesterol, phytosterol, isocholesterol, coprosterol), the *csterols* or natural sterol esters, and the *cholates* (cholic, choleic, glycocholic, taurocholic acids).

The natural lipins of undetermined constitution include chromolipins such as lipochrome, and miscellaneous lipins "of uncertain qualities or doubtful existence."

The artificial lipins include synthetic esters, glycerides, soaps, metallic derivatives of the lipin alcohols (e.g., sodium cholesterylate), compounds of lecithin (e.g., with strychnine), and many other laboratory products.

The sterols and the conjugate lipins are sometimes classified together as lipoids.

<sup>\*</sup> Dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

<sup>†</sup> According to the classification of Rosenbloom and Gies (Biochemical Bulletin, 1911, i, 52), the lipins are divided into natural and artificial lipins.

The natural lipins include aliphatic and carbocyclic lipins, as well as lipins of undetermined constitution.

is related to both the aliphatic and aromatic series. Planer<sup>3</sup> prepared cholesteryl chloride from cholesterol by means of phosphorus pentachloride, while Diels and Abderhalden 4 obtained the same compound by use of thionyl chloride. Lindenmeyer 5 prepared sodium cholestervlate by the action of metallic sodium on a saturated solution of cholesterol in naphtha; while potassium cholesterylate was obtained by Obermüller 6 by the action of metallic potassium on a solution of cholesterol in ether. According to Walitzky,7 cholesteryl chloride reacts with aniline, when their mixture is heated in a sealed tube, and gives rise to cholesteryl aniline; while it reacts with p-toluidine under these conditions to form cholesteryl toluidine. A similar compound is obtained by the action of a naphthylamine or cholesteryl chloride. Bloch 8 heated anhydrous cholesterol with phenyl isocvanate: the product was cholesteryl phenylurethane. Mauthner and Suida 9 subjected a mixture of anhydrous cholesterol and anhydrous cupric sulphate to a temperature of 200°: a mixture of cholestervl ether-dicholestervl oxide-and cholesterilene—a hydrocarbon—was formed; the cholesterilene was removed by solution in benzol, and the ether was recovered from the residue by solution in a mixture of equal parts of benzol and absolute alcohol. These reactions demonstrate that cholesterol is an alcohol; the following reactions prove that it is a secondary alcohol. Diels and Abderhalden 4 oxidized cholesterol to a ketone of the same carbon content, cholestenone, by means of cupric oxide at a temperature of 280-300°. Windaus 10 subjected cholestenone to oxidation by neutral potassium permanganate and obtained a monocarboxylic ketonic acid, the molecule of which contained one atom of carbon less than did the molecule of cholesterol and that of cholestenone. Dorée and Gardner 11 have obtained this monocarboxylic ketonic acid from cholestenone by converting the latter into its ozonide and oxidizing the ozonide with dilute hydrogen peroxide and sulphuric acid.

Cholesterol contains at least one double bond. Wislicenus and Moldenhauer <sup>12</sup> found that, in solution in carbon disulphide, cholesterol adds bromine to form crystalline cholesterol dibromide; while Mauthner and Suida <sup>13</sup> state that cholesterol, in solution in chloroform, adds dry chlorine to form cholesterol dichloride. Lewkowitsch <sup>14</sup> converted cholesterol into choles-

terol-diiodide by means of Hübl's iodine reagent. Mauthner 15 prepared crystalline cholesterol hydrochloride (chlor-cholestanol) by passing hydrogen chloride gas into a solution of cholesterol in a mixture of absolute alcohol and ether. Willstätter and Mayer 16 passed a slow stream of hydrogen through an ethereal solution of cholesterol in the presence of platinum black sponge; each molecule of cholesterol added a molecule of hydrogen and thus gave rise to dihydrocholesterol, which does not add bromine. According to Dorée and Gardner, 11 cholesterol forms a monoözonide. These reactions show the presence of one ethylene bond in the cholesterol molecule; and the investigators, already mentioned, who have prepared the monocarboxylic ketonic acid from cholestenone, point out that the formation of this acid is evidence of the existence of this ethylene bond in a terminal vinyl group of a side chain of the cholesterol molecule. Other reactions indicate the possible existence of more than one double bond in cholesterol. Molinari and Fenaroli 17 found that cholesterol forms a diozonide, while Dorée and Gardner 11 obtained a diozonide of cholestenone. Willstätter and Mayer 16 oxidized dihydrocholesterol with chromic and glacial acetic acids and obtained a ketone,  $\beta$ -cholestanone, which adds bromine.

The molecular formula of cholesterol, according to Mauthner and Suida, <sup>18</sup> is  $C_{27}H_{44}O$ . Windaus <sup>19</sup> gives the molecular formula as  $C_{27}H_{46}O$ , and the structural formula as:

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH} \\ \text{CH}_{2} \\ \text{CH}_{2} \\ \text{CH}_{2} \\ \text{CHOHCH}_{2} \\ \end{array}$$

Of the many esters of cholesterol which have been prepared, the benzoate is of deep interest to the student of quantitative analysis, for Dorée and Gardner <sup>20</sup> have used it in the quantitative determination of cholesterol. Cholesteryl acetate is of value to the bromatologist, for on the melting-point of pure cholesteryl acetate and of pure phytosteryl acetate depends the method of Bömer <sup>21</sup> for the detection of the adulteration of animal fat by means of vegetable fat.

#### ZYMOCHEMISTRY OF CHOLESTEROL.

According to Schultz,<sup>22</sup> a ferment or enzyme, which produces hydrolysis of cholesteryl esters, exists in a mixture of

the whole blood and liver brei of horses and of cattle; the hydrolysis does not occur when either blood-plasma or blood-serum is substituted for whole blood. In connection with enzymes, it is of interest to note that Brücke <sup>23</sup> found that freshly-precipitated cholesterol adsorbs pepsin, a phenomenon which is still utilized in the study of that enzyme.<sup>24</sup>

Since Glikin <sup>25</sup> has reviewed the earlier work on cholesterol, it is necessary to discuss only the more recent work in this place.

## SOLUTIONS OF CHOLESTEROL.

The solutions of cholesterol have recently been studied by several investigators. Porges and Neubauer <sup>26</sup> prepared a colloidal solution of cholesterol in water. Their technique was as follows: A solution of cholesterol in acetone was poured into water carefully and in small portions in order to avoid flocculation. As soon as a somewhat dense cloudiness appeared, the acetone was evaporated at a gentle heat on the water-bath, avoiding too rapid evaporation. This procedure was repeated until a colloidal solution of the desired concentration was obtained; any individual flakes were removed by filtration through thin paper, and a dense, milky, permanent suspension was obtained. The cholesterol behaved as a typical suspension colloid.

Porges and Neubauer <sup>27</sup> have also studied the behavior of alcoholic solutions of cholesterol with alcoholic solutions of metallic salts and of ethereal solutions of cholesterol with ethereal solutions of metallic salts. Since no precipitation occurred under these conditions they consider that cholesterol forms true solutions when dissolved in alcohol and in ether.

Loewe <sup>28</sup> investigated the properties of solutions of cholesterol in organic solvents. Dissolved in chloroform, cholesterol showed the normal behavior of a crystalloid by its influence on the surface tension of the solution; it also elevated the boiling-point of the solution and did not cause foaming. Cholesterol gave rise to a true solution when dissolved in petroleum ether, chloroform, or alcohol, as was shown by the vapor pressure of these solutions. The solutions of cholesterol showed the Tyndall phenomenon, and its solutions in chloroform, carbon tetrachloride, benzol, ether, and petroleum ether, especially when concentrated, contained ultramicroscopic particles, although not in such abundance as did the solutions of other lipoids like

lecithin. Loewe suggests that cholesterol is a semicolloid and should be classified as a semilipoid.

Gies <sup>29</sup> and Rosenbloom <sup>30</sup> have discovered that cholesterol and its esters with benzoic, oleic, palmitic, and stearic acids are able to diffuse from ether through a rubber membrane into ether.

#### CHOLESTEROL AND IMMUNITY.

Cholesterol also plays a rôle in immunity. Free cholesterol prevents the hæmolysis of red blood-corpuscles by saponin. According to the experiments of Windaus,<sup>31</sup> the cholesterol combines with the various saponins and thus exerts an antitoxic action, for the compound of saponin and cholesterol is without hæmolytic power. Thus one molecule of digitonin (a saponin) and one molecule of cholesterol unite to form a stable addition product. Esters of cholesterol are not antitoxic and do not form addition compounds with digitonin. In paroxysmal hæmoglobinuria an autohæmolysin is present in the blood-serum; and Pringsheim <sup>32</sup> has had recourse to intramuscular injections of cholesterol in combating attacks of this disease. Richter <sup>33</sup> has used cholesterol in the treatment of pernicious anæmia.

Robertson and Burnett <sup>34</sup> injected cholesterol into carcinoma of white rats during the premetastatic stage and obtained "a very notable acceleration of the primary growth." During the metastatic stage cholesterol failed to cause an increased growth of the primary tumor, but gave rise to a marked tendency to form metastases and to increase the rate of metastatic growth.

The function of cholesterol as an antigen, in the serum reaction of Wassermann for the detection of Spirochæte pallida, has been studied by Desmouliére.<sup>35</sup> The liver of a syphilitic or of a normal human being—adult or child—or of a pig is ground and rendered lipin-free by extraction with successive portions of ether. The residual tissue is dried in the air, then at 37° C., and is extracted by maceration with absolute alcohol at the latter temperature. The alcoholic extract is removed by filtration and lacks antigenic power: it dissolves cholesterol, which is not precipitated by dilution with physiological salt solution; and the resulting liquid possesses antigenic power to a high degree, giving positive reactions even with the sera of former syphilitics, where the customary Wassermann reaction usually gives a negative result. With sera of non-syphilitics the reac-

tion is always negative. Dextrogyrate isocholesterol also produces complement deviation, when substituted for cholesterol; however, the reaction is far less sensitive than that produced by lævogyrate cholesterol.

## CHOLESTEROL IN THE BLOOD.

During disease the cholesterol content of the blood may change. Grimbert and Laudat <sup>36</sup> state that the total cholesterol of the serum increases during Bright's disease, nephritis, and syphilitic nephritis. It also increases after ingestion of fat in both healthy people and nephritic patients. Weston and Kent <sup>37</sup> report that the total cholesterol of the serum of lunatics does not differ from that of the serum of normal subjects. From the researches of Hermann and Neumann <sup>38</sup> it follows that the whole blood of normal women, of pregnant women, and of newly-born children contains the same quantity of free cholesterol, expressed in grammes per litre. However, the quantity of cholesteryl esters is much higher in pregnant women's whole blood, and much lower in the whole blood of new-born children, than it is in the whole blood of normal women.

## CHOLESTEROL IN THE LOWER ANIMALS.

The occurrence of cholesterol throughout the entire animal world has been studied by Dorée,<sup>39</sup> who found cholesterol in the following animals: rabbit, grass snake, mackerel, whelk, crab, cockroach, earth-worm, and sea anemone. Cholesterollike substances were found in the silkworm moth, starfish, and sponges.

#### PHYTOSTEROL IN METABOLISM.

That the phytosterol of the food can not pass over into the animal fat has been demonstrated by the researches of Virchow <sup>40</sup> on dogs and swine, and of König and Schluckebier <sup>41</sup> on swine. The latter investigators suggest that the phytosterol may be changed into cholesterol within the body, possibly in the intestine. They found that, during certain diets of vegetable origin, a reduction of phytosterol to coprosterol may take place in the digestive tract, and either or both these alcohols may occur in the fæces. Fraser and Gardner <sup>42</sup> have shown that the phytosterol of the food does not appear in the blood stream,

but that a ration containing phytosterol and no cholesterol does give rise to an increase in the quantity of free cholesterol of the blood.

FATE OF CHOLESTEROL IN THE ANIMAL BODY—THE STEROLS OF THE FÆCES.

Many researches have dealt with the absorption and fate of cholesterol in the animal body; certain of these investigations will now be reviewed. In the human digestive tract cholesterol may be reduced to coprosterol, which is a dihydrocholesterolmetameric with the dihydrocholesterol of Willstätter and Mayer. 16 Coprosterol was first isolated from human fæces by Flint,43 who named it stercorin. It was termed coprosterol by von Bondzynski and Humnicki,44 who ascribe its formation to putrefactive processes in the intestine. They found that a healthy man excreted ingested cholesterol in large part as coprosterol in the fæces. A further study of coprosterol has been made by yon Bondzynski. 45 Flint 46 states that only cholesterol is found in the fæces of fasting animals and in the meconium; stercorin is absent. The researches of Müller 47 confirm the view that cholesterol is reduced to coprosterol by intestinal putrefaction. Since an absolute milk diet is one of the best means of limiting putrefaction of protein in the intestine, the excretion of unchanged cholesterol in the fæces of subjects kept on such a diet would demonstrate that the normal reduction of cholesterol to coprosterol is due to intestinal putrefaction. Cholesterol occurred in the fæces of a breast-fed infant, of two bottle-fed infants, of a sucking calf and of two adults on a milk diet, as well as in meconium. Coprosterol occurred in the fæces of an adult on a meat diet and of an adult on a mixed diet. These results strengthen the theory of reduction by intestinal putrefaction. The occurrence of cholesterol in meconium is ascribed to lack of bacterial decomposition in the fœtal intestinal canal.

In the fæces of the horse von Bondzynski and Humnicki <sup>44</sup> discovered hippocoprosterol, which they considered to be a reduction product of cholesterol. Dorée and Gardner <sup>48</sup> have demonstrated that hippocoprosterol is not a product of animal metabolism, but is an alcohol,  $C_{27}H_{56}O$  or  $C_{27}H_{54}O$ , which occurs in grass and passes through the digestive tract unchanged.

They propose for it the name chortosterol. These investigators never found cholesterol in the fæces of herbivora.

In the fæces of the dog von Bondzynski and Humnicki <sup>44</sup> found cholesterol; while Kusumoto <sup>49</sup> states that both cholesterol and coprosterol are present in dog fæces. According to Kusumoto, <sup>50</sup> during a meat diet less cholesterol was excreted in the fæces than was contained in the food; the same result was obtained when cholesterol was added to the ration. The lost cholesterol may be absorbed or may be destroyed by putrefaction. The experiments of Dorée and Gardner <sup>20</sup> show that the dog usually excretes cholesterol of the food as such in the fæces; however, during a diet of raw brains of sheep the cholesterol is excreted as coprosterol.

Ellis and Gardner <sup>51</sup> have studied the excretion of cholesterol in the fæces of the cat. On a meat diet the cholesterol is reduced to coprosterol, but the reduction is not always complete, for a mixture of the two alcohols may be excreted; a portion of the cholesterol disappears in the digestive canal. When cholesterol was added to a ration composed of mixtures of white bread, egg white, wheat germ extracted with ether, and purified suet, cholesterol was excreted unchanged. When phytosterol was added to the ration, unchanged phytosterol was found in the fæces.

#### THE ABSORPTION OF CHOLESTEROL.

Jankau <sup>52</sup> introduced cholestero! into the stomach of rabbits; only a portion of it appeared in the fæces. The remainder must have been absorbed, yet did not appear in the bile and could not be found in the blood several hours after feeding. Injected subcutaneously into rabbits, cholesterol was absorbed, but soon vanished from the blood stream without appearing in the bile. In the case of dogs, cholesterol mixed with the food was well absorbed by the intestine, but did not increase the cholesterol content of the bile. Subcutaneous injection of cholesterol into dogs also failed to increase the cholesterol content of their bile. According to Goodman,<sup>53</sup> intravenous injection of cholesterol into a dog did not increase the total volume of the fistula bile or the total quantity of cholesterol and of cholic acid in the bile. The same investigator found that a diet rich in protein increased the total output of bile, and the total quantity and

concentration of both the cholesterol and cholic acid. A diet of brain, with its high cholesterol content, did not produce any greater excretion of cholic acid in the bile than did a diet of egg albumin, which contains merely a trace of cholesterol. Pribram<sup>54</sup> introduced cholesterol and its esters into the stomach of rabbits and was able to demonstrate that cholesterol was absorbed and occurred in increased quantity in the blood. Moreover, the serum of a rabbit which had been fed cholesterol was able to prevent hæmolysis of red corpuscles by saponin, while the serum of a normal rabbit permitted such hæmolysis; hence, at least the greater portion of the absorbed cholesterol was in the serum and in the free state, since cholesteryl esters do not prevent hæmolysis.

Dorée and Gardner <sup>55</sup> have evolved a theory concerning the cholesterol of the animal body. Cholesterol is a constant constituent of all cells and is not excreted as a waste product on the breaking down of a cell by life process, but is used again in the formation of new cells. The liver breaks down dead cells—for instance, blood-corpuscles—and eliminates their cholesterol in the bile. In the intestine the cholesterol is absorbed, probably as esters, along with the bile-salts, and is carried by the blood for incorporation in new cells. This is opposed to the view of Stadelmann, <sup>56</sup> who maintained that a circuit of the cholesterol with the bile in no case exists.

From experiments, Dorée and Gardner 55 concluded that rabbits excrete cholesterol only when it is fed to them, and that they absorb about one-half of the ingested cholesterol. The dog and the cat also absorb cholesterol from their food. The quantity of cholesterol in the blood of a rabbit was increased by addition of cholesterol to the diet. Fraser and Gardner 57 found that the power of saponin to produce hæmolysis of rabbit ervthrocytes was counteracted by the sera of rabbits which had been fed cholesterol, cholestervl oleate or stearate, or phytosterol; the sera retained their antihæmolytic power after exposure to a temperature of 56° C. for one hour. The serum of a normal rabbit was always used for a control. The experiments demonstrate that ingested cholesterol is absorbed in part and occurs in the blood in the free state; while ingested cholesteryl esters undergo hydrolysis during the process of digestion, and their cholesterol appears, at least in part, in the blood stream in the free state. The amount of cholesterol which found its way into the blood stream was not increased by increasing the quantity of it in the ration; hence, the rabbits probably absorbed only so much cholesterol as they could utilize. A further study by Fraser and Gardner <sup>42</sup> has revealed the rôle of phytosterol in increasing the antihæmolytic power of the serum. When rabbits are fed a cholesterol-free diet containing phytosterol (ordinary bran), phytosterol does not appear in the blood as such, but the quantity of free cholesterol in the blood increases. Both the free cholesterol and the cholesteryl esters are greater in quantity in the blood of rabbits fed ether-extracted bran plus cholesterol than in the blood of rabbits fed only the extracted bran. The ingested cholesterol gives rise to an increase in both the free and esterified cholesterol of the blood.

Ellis and Gardner have studied the influence of various diets and of inanition on the cholesterol content of the liver 58 and of other organs 59 of rabbits. A diet of green food containing phytosterol gave rise to a slight increase in the cholesterol content of the liver. The total quantity of cholesterol in the liver underwent a marked increase on a diet of ether-extracted bran plus cholesterol, and also after intraperitoneal injection of cholesterol. During inanition the rabbits lived on their own tissues and stored cholesterol in their livers, while the content of their blood in both free and total cholesterol underwent an increase. The cholesterol content of the blood of rabbits depended on the sterol content of their food. In the case of muscle, kidney, and lung, the quantity of cholesterol was apparently independent of the sterol content of the diet. Starvation caused an increase in both total and esterified cholesterol of the kidney; while intraperitoneal injection of cholesterol gave rise to an abnormally high content in cholesteryl esters in that organ. Inanition, as well as intraperitoneal injection of either olive oil or olive oil plus cholesterol, led to an increase in the total cholesterol content of the bile.

#### CHOLESTEROL IN INCUBATION AND AUTOLYSIS.

Ellis and Gardner <sup>60</sup> determined the total quantity of cholesterol in eight individual eggs, eight individual chicks, a set of six eggs and a set of six chicks. The chicks were freshly hatched. The analyses failed to reveal any gain in cholesterol

during incubation. "In the differentiation of the ovum into the complex aggregates of cells constituting the chick no formation of cholesterol takes place."

Corper <sup>61</sup> has studied the influence of autolysis upon cholesterol. During the autolysis of dog spleen the cholesterol in that organ is not changed.

#### CHOLESTEROL IN PATHOLOGY.

Windaus <sup>62</sup> has demonstrated that the free cholesterol content of normal and pathological (amyloid or fatty-degenerated) human kidneys is about the same, but that the diseased kidney contains far more cholesteryl esters (oleate and palmitate) than are present in the normal kidney.

Duranton 63 has made an extensive study of the action of microörganisms on ox bile with special reference to the deposition of cholesterol. After filtration and sterilization, portions of the bile were sown with pure cultures of the organisms in bouillon and incubated at 37° C. Sterile control experiments were also carried out. B. coli, B. typhosus of Eberth, two strains of B. paratyphosus, B. diphtheriæ of Löffler, B. pyocyaneus, B. subtilis, and Staphylococci produced precipitates in which cholesterol crystals were present. B. pyocyaneus caused the deposition of crystals as early as the fifteenth day; while in the case of Staphylococci the crystals appeared on the sixtieth day. Under anaërobic conditions, B. tetani, B. putrificus, B. coli, and B. pyocyancus gave rise to a deposit of cholesterol crystals. B. coli and B. pyocyancus precipitated the cholesterol more rapidly under anaërobic conditions than in an aërobic environment. The appearance of cholesterol crystals was always preceded by the formation, in the culture-tubes, of a precipitate which responded to Pettenkoffer's reaction and, therefore, consisted of bile-acids. However, B. paratyphosus and B. coli did not modify the alkalinity of the bile; B. typhosus and B. diphtheriæ diminished the alkalinity to but a very slight extent; and B. pyocyaneus increased the alkalinity in a high degree. B. typhosus, B. coli and B. pyocyaneus were grown on bile for two days; the cultures sterilized in the autoclave at 100° C. for fifteen minutes and then returned to the incubator. No precipitates were formed, proving that the microörganisms do not act mechanically as foreign bodies, causing a precipitation of cholesterol from the bile. The toxins of B. diphtheriæ, B. tetani, B. typhosus, and B. coli were permitted to act on bile; the precipitate formed more rapidly than when bouillon cultures of the organisms themselves were used, and cholesterol crystals were always present, although not so plentifully as in the experiments with the living organisms.

Duranton concludes that under the influence of microorganisms decomposition of the bile-salts occurs, accompanied by a diminution of the quantity of bile-acids. Since the bile no longer contains sufficient bile-salts to hold the cholesterol in solution, the latter is precipitated. Most microörganisms possess this power, and apparently act by means of their toxins to decrease the content of the bile in bile-salts. In the formation of biliary calculi *in vivo* the leading rôle is played by microorganisms which have gained entrance to the bile and give rise to a precipitation of its cholesterol. The epithelial cells present play an entirely secondary rôle in the formation of calculi by acting as centres for the deposition of the cholesterol as it is precipitated.

Crystals of cholesterol have been found in the urinary sediment in cases of cystitis, pyelitis, chyluria, and nephritis.<sup>104</sup>

The influence of the subcutaneous injection of toluylene diamine (1 methyl 2, 4 diamino benzene) upon the excretion of cholesterol in the bile 64 and fæces 65 of dogs has been studied by Kusumoto. The quantity of cholesterol was increased, due to the increased destruction of red blood-corpuscles in the liver under the influence of the diamine.

# NATURAL OCCURRENCE OF OXIDATION PRODUCTS OF CHOLESTEROL.

Lifschütz <sup>66</sup> has prepared oxidation products of cholesterol by permitting a solution of potassium permanganate in concentrated acetic acid to act upon a solution of cholesterol in glacial acetic acid at the temperature of the water-bath. Among the products of the reaction are oxycholesterol ether and oxycholesterol. If the formula of cholesterol be written  $C_{26}H_{44}O$ , then oxycholesterol ether is  $(C_{26}H_{43}O)_2O$  and oxycholesterol is  $C_{26}H_{44}O_2$ . Each of these compounds dissolves in glacial acetic acid and then reacts with concentrated sulphuric acid to give a solution with a characteristic absorption spectrum. In the case

of oxycholesterol ether the absorption spectrum is characterized by a broad, deep-black band covering the entire yellow and part of the green and by a fine line in the red; while in the case of oxycholesterol it is characterized by a band in the red. Lifschütz <sup>67</sup> has also obtained these oxidation products of cholesterol by the action of benzoyl peroxide on the solution of cholesterol in glacial acetic acid, and has demonstrated their presence in wool fat,<sup>66</sup> in brain and in pancreas fat,<sup>67</sup> in bone fat and in the fat of fresh whole blood of cattle,<sup>68</sup> and in the fresh defibrinated blood of cattle.<sup>69</sup>

#### CHOLESTEROL AND THE BILE-ACIDS.

The relation of cholesterol to the bile-acids, cholic, choleic, taurocholic, and glycocholic acids, was first suggested by Berthelot,<sup>2</sup> and has recently been discussed by Goodman <sup>53</sup> and by Rosenbloom and Gies.<sup>70</sup>

### II. THE PREPARATION OF CHOLESTEROL.

### DESICCATION OF THE TISSUE.

Tissues, such as brain, must be dried before cholesterol can be extracted from them. Various procedures have been devised to prepare the tissues for extraction. Baumstark 71 removed the water from brains of horses, calves, sheep, and cattle by permitting the brains to remain in contact with ether, which was changed at intervals. The water was removed by diffusion, but the process required several months. The brains were then cut in slices one centimetre thick, and were extracted in the cold with ether for a period of two months. Bünz 72 mixed finelydivided horse brains with one and one-half times their quantity of anhydrous sodium sulphate and ground the resulting mass to a fine powder, which was extracted in the cold with ether. Rosenheim 73 mixed minced sheep brain with sand and three times its weight of plaster of Paris, permitted the mass to set, crushed it to a coarse powder, and extracted in the cold with acetone. Tebb 74 applied the method of Rosenheim to human brains. Fränkel and Elfer 75 mixed the tissue brei in a mortar with one-half its weight of anhydrous disodium monohydrogen orthophosphate at a temperature of about 40° C., transferred the mixture to a warm cloth, which was then placed in a warm

Vol. CLXXVI, No. 1054-30

press in order to remove the liquid hydrated sodium phosphate—Na<sub>2</sub>HPO<sub>4</sub>.12H<sub>2</sub>O—which had been formed at the expense of the tissue water and which melts at 35° C. The solid residue was permitted to cool, powdered, and extracted with petroleum ether. Rosenbloom <sup>76</sup> has quite recently recommended the use of calcium carbide as a dehydrating agent in the preparation of cholesterol from brain.

#### REMOVAL OF PHOSPHATIDES.

Zuelzer,<sup>77</sup> who worked on ox brain, devised a method for the separation of cholesterol from lecithin and other phosphatides. When an ether extract of brain, not too dilute, was treated with acetone until a precipitate no longer formed, the phosphorized compounds had been precipitated, while the cholesterol remained in solution in the mixture of ether and acetone.

### SAPONIFICATION OF GLYCERIDES.

Baumstark <sup>71</sup> stated that the greater portion of the cholesterol is present in the brain in the combined state; the later work of Bünz <sup>72</sup> and of Tebb <sup>74</sup> has shown that the cholesterol of that organ is present entirely in the free state; and, in harmony with this, Ellis and Gardner <sup>59</sup> have proved that only free cholesterol and no cholesteryl esters exist in the brain of the rabbit. However, during the extraction of cholesterol, fats are also extracted and accompany the cholesterol even after the precipitation of the lecithin. These fats are best removed by saponification, and two reagents are available for this purpose—alcoholic potash and true sodium ethylate. Chevreul used boiling alcoholic potash for the saponification of glycerides, and the use of this reagent in fat chemistry has been emphasized by Koettstorfer.<sup>78</sup>

The use of sodium ethylate was introduced by Kossel and Obermüller;<sup>79</sup> in this mode of saponification the entire reaction is completed *in the cold*, at the temperature of the room, and therefore the new method has a marked advantage over the use of boiling alcoholic potash. Kossel and Obermüller state that, on addition of an alcoholic solution of sodium ethylate to the solution of a fat in ether, in a very short period of time—from several seconds to several minutes—a compact precipitate of the sodium soaps of the fatty acids is formed. If sufficient

sodium ethylate has been used, the saponification is completed in a short time at ordinary temperature and the soap separates in the form of a precipitate which may be removed without difficulty by filtration. The filtrate contains the cholesterol. The mixture should be permitted to stand for twenty-four hours before filtration. If either the quantity of sodium ethylate or the period of reaction be insufficient, new precipitates of soap are formed after filtration. It was ascertained by experiment that from 100 to 150 grammes of fat require for saponification approximately so much sodium ethylate as is formed by solution of 10 grammes of metallic sodium in 150 to 200 c.c. of absolute alcohol. It is recommended to use two-fold or three-fold this quantity of ethylate in a saponification.

Kossel and Krüger so have modified this procedure. They dissolve the fat in absolute alcohol and heat with the alcoholic solution of sodium ethylate on the water-bath, in order to hasten the saponification. The quantity of ethylate required for actual complete saponification of any given weight of fat is the quantity theoretically required by that weight of fat. If the reaction be carried out under a reflux condenser instead of in a vessel exposed to the atmosphere, either the period of the reaction must be lengthened or the quantity of ethylate must be increased in order to insure complete saponification of the fat. Kossel and Krüger always use a freshly-prepared solution of sodium ethylate, obtained by dissolving metallic sodium in absolute alcohol; each 100 c.c. of the solution contains 5 grammes of sodium; 5 grammes of fat require from 10 to 15 c.c. of this solution for their saponification.

Obermüller <sup>81</sup> has studied the mechanism of the reaction which occurs when sodium ethylate saponifies a glyceride. When the fat is dissolved in ether or in alcohol and is treated with an alcoholic solution of sodium ethylate, sufficient water must be present in order to produce saponification of the fat; otherwise the reaction does not occur at all or is incomplete. This water may be present in the alcohol (absolute alcohol contains but 99.4 to 99.8 per cent. of alcohol) or may be absorbed from the atmosphere. The fatty acid glyceride enters into a double decomposition with the sodium ethylate to form the ethyl ester of the fatty acid and the sodium salt of glycerol. The water decomposes the sodium salt of glycerol, and the products of the reac-

tion are glycerol and sodium hydroxide. The sodium hydroxide and the ethyl ester of the fatty acid now react to form ethyl alcohol and the sodium salt (soap) of the fatty acid. The reaction is most rapid with sodium ethylate, less rapid with sodium amylate, and still less rapid with sodium methylate—which may also be used for the saponification of fats.

#### CHOLESTEROL FROM BRAIN.

At some stage of the preparation of cholesterol heat has always been used—either during the extraction, or for the evaporation of the solvent, or during saponification for the removal of fatty matter. In the course of this research cholesterol has been prepared from brain in two ways: (a) During extraction and purification the temperature has never exceeded that of the body; (b) during the course of extraction and purification the temperature has exceeded that of the body only during the process of saponification by means of boiling alcoholic potash.

## Preliminary Experiment.

Twenty-four brains from freshly-killed sheep, and retaining the animal heat, were cut into slices five millimetres in thickness by means of a sharp knife; the sliced brains were spread out in porcelain dishes and covered with alcohol; they were moved about and turned over from time to time in order to expose fresh surfaces to the dehydrating action of the alcohol. The alcohol was twice decanted, and replaced by a new portion, during the course of thirty-six hours. The brains were then dried between filter-paper and ground fine in a meat-chopper. The minced material was placed in a glass-stoppered bottle of ample size, covered with an excess of ether, and allowed to extract at the temperature of the room for a period of twentyfour hours, shaking at intervals. The ether was removed by decantation through a folded filter, and the insoluble material was permitted to drain on the filter. The residue was again extracted with ether for a period of twenty-four hours, and the insoluble residue from this extraction was subjected to a third extraction for the same period of time. Thus three ether extracts were obtained. Each of these was heated on the waterbath in order to remove the solvent, but the temperature had risen far above 37° C. long before all the solvent had vanished;

in fact, the full temperature of 100° C. was required to obtain a dry residue. The brains had retained alcohol and given it up to the ether.

Heating was therefore abandoned in the subsequent experiments. In order, however, to test the methods of purification—which will be described in detail in the section on "Preparation of Pure Cholesterol from Brain," and which will be outlined in Table III—the residues of the first and third extracts were studied separately. Each was dissolved in ether, the lecithin and its related compounds were precipitated by acetone and removed by filtration, and the filtrate was evaporated before an electric fan. The residue was divided into two equal portions, from one of which the fat was removed by saponification with alcoholic potash; from the other by saponification with sodium ethylate. The cholesterol thus obtained was further purified by recrystallization at room temperature from ether to which a small amount of alcohol had been added.

In the case of the first extract, the fraction saponified by alcoholic potash, as well as the fraction saponified by sodium ethylate, gave a deposit of crystals on both the bottom and the sides of the crystallizing dish. Far more lipochrome was present in the crystals on the side than in those on the bottom of the dish. The deposit of crystals on the side was removed by means of a scalpel, and it and the deposit on the bottom were recrystallized separately at room temperature from ether containing alcohol until pearly-white crystals—free from lipochrome—were obtained.

In the case of third extract, mechanical separation of the first crop of crystals into two fractions was not necessary. After saponification with alcoholic potash, the entire product was pure on the second crystallization. After saponification with sodium ethylate, pearly plates were deposited on the bottom of the dish on the fourth crystallization, while the lipochrome was concentrated in a slight crust of crystals on the side of the dish; this crust was discarded.

Of course, the mother liquors of the various crystallizations contained the major portion of the lipochrome, as well as of any aldehyde resins, formed by the action of the alkali on the alcohol during the process of saponification. The crystals were freed from mother liquor by washing with alcohol, and were

dried on filter-paper. The melting-point of each final product was determined with ordinary thermometers and corrected according to the formula of Bömer.<sup>21</sup> In Table I the corrected melting-points are given.

TABLE I.

MELTING-POINT OF CHOLESTEROL.

Preliminary Experiment.

Extract	Mode of saponification	Number of crystallizations	Corrected melting point, °C.
FIRST	Alcoholic potash $\left\{ \begin{array}{c} \\ \\ \\ \end{array} \right.$ Sodium ethylate $\left\{ \begin{array}{c} \\ \\ \end{array} \right.$	Bottom deposit crystallized twice. Side deposit crystallized thrice. Bottom deposit crystallized twice. Side deposit crystallized twice.	147.6 147.5 147.0
THIRD	Alcoholic potash Sodium ethylate	2 4	147.7 147.3

## Preparation of Pure Cholesterol from Brain.

The reagents used in these experiments will first be described. Alcohol was freshly-redistilled 95 per cent. alcohol. Alcoholic potash was a 4 per cent. solution of C. P. potassium hydroxide in alcohol; the hydroxide was ground to a fine powder in a mortar, then mixed with the alcohol; after several days the slight quantity of insoluble matter was removed by filtration through a folded filter. The filtrate was unusually pure; for a period of over three months it remained water-white without the faintest trace of yellow. Sodium ethylate was prepared as required by dissolving bright metallic sodium in absolute alcohol—ten grammes of metal to each 150 c.c. of solvent. Ether was absolute ether, redistilled over sodium. Acetone was redistilled as required, and the fraction boiling at 56 to 57° C. was collected for use. Hardened, smooth filter-papers were always used for filtrations.

Sheep brains, in sets of twenty-four, still retaining the animan heat, were cut, dehydrated with alcohol, and extracted with ether at the temperature of the room, as described in the preliminary experiment. Each set of brains gave rise to a series of three extracts. Four sets of brains were worked up: there-

fore twelve extracts were obtained. Each extract was placed in a flat-bottomed porcelain dish, which was slightly inclined toward an electric fan, so that the current of air generated by the fan would play over the surface of the liquid. As soon as a crust formed over the surface of the solution it was broken up with a glass rod. As evaporation advanced, the angle of inclination of the dish was increased; and when the solvent had entirely evaporated, the dish was placed at an angle of almost ninety degrees to the table in order to dry the residue, which was stirred with a glass rod to assist in the process. The residues consisted of yellowish semisolid masses. Each residue was transferred to a glass-stoppered bottle by means of a horn spatula. The four residues of the first extracts were finally combined, as were the four residues of the second extracts and the four residues of the third extracts. Thus three masses of lipins were obtained, each of which was derived from ninety-six sheep brains. Each mass was triturated in a mortar with successive portions of ether until it had been completely dissolved; as little ether as possible was used so that the solution would be practically saturated with lipins. The ethereal solution was transferred to a tall glass cylinder, and three-fold its volume of acetone was added slowly with constant stirring in order to precipitate the lecithin and its related substances. The mixture was permitted to stand over night. In the case of the first extract, the supernatant liquid was perfectly clear; in the case of the second extract and of the third extract, the supernatant liquid held in suspension minute particles; but in all three cases, after filtration through a folded filter, the filtrate was perfectly clear. The first extract yielded the most deeply colored filtrate, the third extract the least colored filtrate, while the color of the filtrate of the second extract lay between that of the other two.

Each filtrate was evaporated to complete dryness before an electric fan, the residues of crude cholesterol forming solid masses. The ninety-six brains had weighed 8294 grammes; the total weight of each of the three ether extracts, the weight of each residue of crude cholesterol, and its saponification number are given in Table II. Of each residue, one gramme was used for the determination of the saponification number; the remainder was divided into two equal portions, both of which were used for the preparation of pure cholesterol—one after saponi-

fication by means of sodium ethylate; the other after saponification by means of alcoholic potash. The saponification number (number of milligrammes of potassium hydroxide required for the saponification of one gramme of the crude cholesterol) was determined in the usual way by the method of the Association of Official Agricultural Chemists,82 but, on account of the small weight of the sample, 0.4 per cent. alcoholic potash and 0.2 normal mineral acid were substituted for 4 per cent. alcoholic potash and 0.5 normal acid. The saponification numbers show that considerable saponifiable matter was present in all the residues; and, as was to be expected, the residue derived from the first extract had a higher saponification number and therefore contained more saponifiable matter than the residues derived from either of the other extracts. Each of the two modes of saponification for the preparation of pure cholesterol will now be described.

TABLE II.

ETHER EXTRACT OF SHEEP BRAIN.

8294 Grammes of Brain.

	Ether	extract	Crude ch	Saponifica- tion number of crude cholesterol	
Extract	Weight in grammes	Per cent. of fresh tissue	Weight in grammes Per cent. of fresh tissue		
FIRST. SECOND. THIRD.	260 173 104.5	3.13 2.09 1.26	40.0 27.5 18.0	0.48 0.33 0.22	36.2 25.6 27.7

## Saponification by Means of Alcoholic Potash.

The crude cholesterol was placed in an Erlenmeyer flask, and for each gramme of material 10 c.c. of alcoholic potash were added. The flask was heated on a water-bath beneath a reflux air condenser, and the solution was boiled for one hour after all the crude cholesterol had dissolved. As the contents of the flask cooled to the temperature of the room, a voluminous precipitate of crystalline cholesterol separated. The crystals were removed by filtration, the filtrate was transferred to a separatory funnel, diluted with three or four times its volume of water, and shaken with an ample volume of ether. After the mixture had separated into two layers, the aqueous layer was drawn off and again extracted with ether. The two ethereal

extracts were combined, and in them was dissolved the precipitate of cholesterol. The ethereal solution was washed with water in a separatory funnel, then evaporated before an electric fan. After the ether had disappeared completely, considerable alcohol was left in the porcelain dish. The cholesterol and this alcohol were transferred to an Erlenmeyer flask and the process of saponification was repeated. In order to avoid contamination of the ether with much alcohol, after filtering out the cholesterol crystals, the alcoholic filtrate was concentrated in a casserole on the water-bath to a volume of 25 c.c., diluted with 125 c.c. of water, and extracted with two successive portions of ether in a separatory funnel. The combined ether layers were used for dissolving the crystalline cholesterol, and the resulting ethereal solution was washed free from soaps by successive portions of water in a separatory funnel. A solution of calcium nitrate was used in testing portions of the wash waters for the presence of soaps. The wash waters were combined and extracted with ether, which was then washed free from soaps by means of water; this ether was then added to the main ether solution. The ether was permitted to evaporate spontaneously in the room. The residue was dissolved in as small a volume of ether as possible; the solution was filtered into a small crystallizing dish; the filter was washed with ether: a few cubic centimetres of absolute alcohol were added to the contents of the dish, which was covered with a watch-glass; and the solvent was allowed to evaporate slowly and spontaneously at room temperature. When the mother liquor amounted to about one-eighth of the volume of the original solution it was poured on a filter-paper on a Buchner funnel, the crystals were transferred to the filter, sucked free from mother liquor, and washed with alcohol. The crystals thus obtained were again subjected to the process of crystallization, and the entire procedure was repeated until a crop of crystals was obtained entirely free from lipochrome. These crystals were filtered and washed as described above, then placed on a pad of smooth filter-paper, beneath a bell jar, and permitted to dry in the air at the temperature of the room.

Saponification by Means of Sodium Ethylate.

The crude cholesterol was dissolved in ether in Erlenmeyer flasks of 500 c.c. capacity; in every case sufficient ether was

taken to insure at least three volumes of ether to one volume of ethylate solution in the final mixture. For each gramme of crude cholesterol, 3 c.c. of ethylate solution were used. This reagent was slowly added to the ethereal solution, the flask being given a rotary motion during the mixing. The contents of the flask were shaken at frequent intervals in the course of the first hour, and it was then permitted to stand for twenty-four hours. Even in the first few minutes after adding the reagent the saponification became apparent by the precipitation of soaps. supernatant liquid was decanted through a filter on a Buchner funnel; the precipitated soap was also transferred to the filter and sucked free from solvent. It was then finely divided, shaken up with ether, and the washings thus obtained were filtered through a paper on the Buchner funnel and added to the filtrate from the soaps. The combined filtrate and washings were diluted with ether, and were washed with water several times in a separatory funnel in order to remove alcohol and soaps. wash waters were combined and shaken with ether to recover any cholesterol; the ether was added to the main ethereal solution, which was now evaporated to dryness before an electric fan. The residue was dissolved in other and treated with sodium ethylate as before. The small quantity of precipitated soaps was removed by filtration with the aid of a Buchner funnel, and the precipitate was washed on the filter with ether. The combined filtrate and washings were diluted with ether and were shaken with successive portions of water in a separatory funnel, until a portion of the wash water failed to vield a precipitate on the addition of a solution of calcium nitrate—thus showing that soaps had been completely removed from the ethereal solution. The combined wash waters were extracted in a separatory funnel with ether in order to recover cholesterol; the ether was washed with water until free from soaps, and was combined with the main ethereal solution, which was then evaporated to dryness before an electric fan. The residue was reddish-vellow in color and vielded a reddish-vellow ethereal solution; the color was much deeper than that of the residue obtained after saponification with alcoholic potash. This residue was recrystallized from ether at the temperature of the room, in the same manner as has already been described in detail in the latter portion of the preceding paragraph ("Saponification by Means of

#### TABLE III.

#### PREPARATION OF PURE CHOLESTEROL FROM PHOSPHATIDE-FREE ETHER EXTRACT OF BRAIN.

Phosphatide-free Residue of the Ether Extract.

Saponify with alcoholic potash Cool and filter

Crystals of cholesterol Dissolve in ether extract of mother liquor

Mother liquor Dilute with water, extract twice with ether

Ether layers

Aqueous layers discarded

Wash with water

Aqueous Ether layer layer discarded

Evaporate before electric fan

Saponify residue with alcoholic potash, cool and filter

Crystals of cholesterol Dissolve in ether Mother liquor

Concentrate on waterbath, dilute with water, extract of mother liquor extract twice with ether

> Ether layers Aqueous layers discarded

Wash with water until free from soaps

Combined aqueous layers

Ether layer

Extract with ether

Aqueous layer discarded.

Ether layer. Wash with water until free from soaps

Aqueous layer discarded

Ether layer

Evaporate spontaneously in room

Recrystallize residue from ether at room temperature until free from lipochrome Dissolve in ether, saponify with sodium ethylate, filter, wash with ether

On filter soaps discarded

Filtrate and ethereal washings Dilute with ether. wash with water several times

Ether layer

Aqueous layers combine and extract with ether

Aqueous Ether layer layer

discarded Evaporate before electric fan

> Dissolve residue in ether, saponify with sodium ethylate, filter out soaps, wash with ether

On filter soaps discarded Filtrate and ethereal washings Dilute with ether, wash with water until free from soaps

Aqueous layers combine and extract with ether

Ether layer

Aqueous Ether layer layer discarded

Wash free from soaps with water

Aqueous layer discarded

Ether layer

Evaporate before electric fan

Recrystallize residue from ether at room temperature until free from lipochrome

Alcoholic Potash"), until at last crystals free from lipochrome were obtained.

The two methods are outlined in Table III.

A set of three preparations of cholesterol from brain was thus obtained from the first, second, and third ether extracts, respectively, by means of saponification with boiling alcoholic potash; another set of three preparations was obtained from these three ether extracts by means of saponification with sodium ethylate at the temperature of the room. The filtrates and washings from all six of these preparations were combined. After the evaporation of the ether, a voluminous precipitate of cholesterol deposited, which was removed from the supernatant alcohol by filtration, washed with a small quantity of alcohol, and recrystallized from ether, in the manner already described, until the crystals were entirely free from lipochrome. (G, Table IV.)

The melting-point of each preparation was determined by means of thermometers, certified by the United States Bureau of Standards, and was corrected by the formula of Bömer: <sup>21</sup>

S-Corrected melting-point.

T—Observed melting-point.

t—Mean temperature of the air, surrounding the projecting mercury column, ascertained by means of a second thermometer, which records the temperature of that column at a point midway between the surface of the liquid in the bath and the point T of the first thermometer.

n—The length, in thermometer degrees, of the column of mercury of the first thermometer projecting above the surface of the bath.

$$S = T + 0.000154n \ (T-t).$$

The melting-points of the samples of cholesterol obtained from brains, as well as of those obtained from gall-stones, are given in Table IV. For purposes of comparison, the melting-points of certain mixtures of these preparations are also included in that table. The results will be discussed after a description has been given of the preparation of cholesterol from gall-stones (H and I, Table IV).

## Cholesterol from Gall-Stones.

Twelve grammes of gall-stones, varying in size from that of a grain of rice to that of a shell-bark, were obtained from human cadavers, and were ground to a fine powder in a mortar. The powder, which possessed a reddish-brown color, was extracted with 300 c.c. of absolute ether at the temperature of the room, shaking at intervals, for a period of twelve days. The ethereal solution was poured through a filter and the residue of bilepigments was washed with absolute ether. The filtrate and washings were combined and permitted to evaporate spontane-

TABLE IV.

MELTING-POINTS OF PREPARATIONS OF PURE CHOLESTEROL AND OF MIXTURES OF THESE PREPARATIONS.

Sample	Source	Mode of saponification	Num- ber of crys- talliza- tions	Quantity obtained, grammes	Correct- ed melt- ing- point °C.	Crystal form
A	Desir feet on					
Α	Brain, first ex-	Alcoholic potash	2	9.4	149.1	Plates
В	Brain, second extract					
С	Brain, third ex-	Alcoholic potash	2	4.5	148.5	Plates
D	tract Brain, first ex-	Alcoholic potash	2	3.5	149.0	Plates
	tract	Sodium ethylate	3	8.2	149.1	Needles
Е	Brain, second extract	Sodium ethylate				
F	Brain, third ex-	Sodium emyrate	3	6.5	148.7	Plates
G	tract Brain, mother	Sodium ethylate	4	2.9	148.4	Needles
	liquors of A		1			
H	Gall-stones		2 I	6.7 5.4	147.1 147.4	Needles Needles
I A = loop C	Gail-stones		2	4.3	147.4	Plates
A plus C, 50 per cent.						
of each					147.8	
D plus F, 50 per cent.						
of each					147.7	
A plus D, 50 per cent.						
of each					148.0	
A plus H, 50 per cent.						
of each			. /		147.8	
		· · · · · · · · · · · · · · · · · · ·			- 1	

ously at room temperature from a crystallizing dish which was covered with a watch-glass. The major portion of the cholesterol deposited on the sides of the dish as a mass of needles, pearly-white in color, save at the top, where a yellow rim appeared; a scanty yellowish deposit also formed on the bottom

of the dish. The yellow portion was removed from the deposit on the sides of the dish by means of a scalpel, and the pure white material was preserved as sample H. The yellow portion was combined with the deposit on the bottom of the dish, and then recrystallized from absolute ether plus a few cubic centimetres of alcohol until free from lipochrome, in the manner already described in the preparation of cholesterol from brain; sample I was thus obtained.

#### DISCUSSION OF THE RESULTS.

Upon reference to Table IV it is seen that the melting-point of all six of the samples prepared from brain—A to F, inclusive—is practically the same; the difference between the extreme values is but 0.7° C. From this fact the conclusions are naturally drawn: The cholesterol obtained from the first, from the second, and from the third extract of brain is one and the same chemical individual, free from any contaminating body, for any contaminant would have accumulated in either the first or the third extract, and demonstrated its presence by its influence on the melting-point. The heating during the process of saponification with boiling alcoholic potash does not produce any rearrangement of the molecule of cholesterol, for if such a change occurred the melting-point of the compound obtained by saponification with alcoholic potash would differ from that of the compound obtained by saponification with sodium ethylate at a temperature never exceeding that of the body.

As might be expected, the melting-point of the cholesterol, sample G prepared from the mother liquors, was somewhat lower than that of the other six samples, for any compounds which had accompanied the cholesterol from the brain and had passed into the mother liquors would tend to contaminate the cholesterol derived from those liquors and to depress its melting-point.

The cholesterol from gall-stones melted at a slightly lower temperature than did the first six samples from brain, yet the figures lie so close that they bear witness to the identity of the cholesterol from the two sources. Moreover, the melting-point of the material from gall-stones lies above that of the cholesterol G, from the mother liquors of the brain preparations.

The melting-points of the mixtures also command attention. Equal quantities by weight of two samples were ground intimately in a mortar, and the melting-point of the mixture was determined. When two masses have the same melting-point, and are mixed intimately in equal proportions by weight, if the two masses are the same chemical individual in a state of purity the melting-point of this mixture will vary but slightly, if at all, from that of either of the mixed masses. However, if the two mixed masses are different chemical compounds, by the law of Raoult the melting-point of this mixture will be far below that of either of the two constituent masses. The melting-points of the mixture of samples A and C and of the mixture of samples D and F bear witness that the cholesterol of the first and of the third extract—and therefore, by inference, of the second extract is one and the same chemical individual. The melting-point of the mixture of samples A and D again shows that no rearrangement of the cholesterol molecule is brought about by the heat during the saponification with alcoholic potash, and that both modes of saponification yield the same cholesterol. The meltingpoint of the mixture of samples A and H proves the identity of cholesterol from brain and that from gall-stones.

Lastly, the melting-point of the mixture of samples A and H, combined with the fact that the melting-points of the samples prepared from gall-stones lie so very close to the melting-points of the samples prepared from brain, gives evidence that neither potassium hydroxide nor sodium ethylate gives rise to a rearrangement of the cholesterol molecule. The cholesterol from gall-stones was never in contact with either of these alkaline reagents, yet it is exactly the same chemical compound as the cholesterol from brain in the preparation of which one of these two reagents was always used.

To sum up, the data for melting-points demonstrate the uniform purity of all the samples of cholesterol and also prove that all these samples are one and the same chemical compound.

For purposes of comparison, it may be mentioned that, according to Bömer,<sup>21</sup> the corrected melting-point of cholesterol lies between 148.4° and 150.8° C., while Polenske <sup>90</sup> has determined the corrected melting-point of 254 samples of cholesterol from lard with the following results:

Number of samples	Corrected melting-point, °C.
2	145
15	146 -146.5
36	146.5-147
185	147 -148
15	148
I	148.5

# III. CHOLESTEROL AND THE IODINE REAGENTS FOR FAT ANALYSIS.

In the course of the introduction to this dissertation certain reactions were discussed which demonstrate the presence of at least one, and possibly of two double bonds, in the molecule of cholesterol. The addition compounds of cholesterol, including those with halogens and haloid acid, were described. Certain of these compounds have found application in the analytical chemistry of cholesterol. Thus von Bondzynski and Humnicki 44 devised a method for the separation of cholesterol and coprosterol, which depends on the fact that cholesterol is converted by bromide into cholesterol dibromide, a compound insoluble in petroleum ether, while coprosterol is not acted on by bromine and is readily soluble in petroleum ether. Windaus 83 has separated cholesterol and phytosterol by means of the difference in solubility of their dibromides in ice-cold glacial acetic acid, which dissolves phytosterol dibromide, while cholesterol dibromide is insoluble.

The iodine number of cholesterol has also been determined. Lewkowitsch <sup>14</sup> obtained 68.09 and 67.3 by the method of Hübl; Marcusson <sup>84</sup> obtained 29.4 by the method of Waller and 109.4 by the method of Wijs.

For the determination of the iodine number, which is a measure of the unsaturated or double bonds, four methods exist—those of Hübl, <sup>85</sup> Wijs, <sup>86</sup> Hanus, <sup>87</sup> and Waller, <sup>88</sup> The last method is comparatively unimportant. Hübl used a solution of iodine plus mercuric chloride in 95 per cent. alcohol. Waller added 5 per cent. of hydrochloric acid of specific gravity 1.19 to this solution, and also used as a solvent alcohol into which hydrogen chloride had been passed. The reagent of Wijs was a solution of iodine monochloride in 95 per cent. acetic acid; that of Hanus a solution of iodine monobromide in glacial acetic acid. In this research the reagents of Hübl and Hanus were

prepared and used as directed by the Association of Official Agricultural Chemists; <sup>89</sup> the reagent of Wijs contained iodine monochloride in exactly the same molecular concentration as that of iodine monobromide in the reagent of Hanus. Ten cubic centimetres of chloroform were always used as a solvent for the cholesterol. The o.i normal sodium thiosulphate, for titration of the unabsorbed iodine, was standardized against potassium permanganate which had just been checked with ferrous ammonium sulphate. The results obtained by these three methods are collected in Table V. For a full description of each sample of cholesterol, reference should be made to Table IV.

TABLE V.

IODINE NUMBER OF CHOLESTEROL.

Experi- ment number	Sample of cholesterol	Weight of cholesterol	Iodine number	Volume of iodine reagent	Name of iodine reagent	Period of absorption
1 2 3 4 5 6 7 8 9 10	D D D D D D D D D D D D D D D D D D D	0.1010 0.1021 0.2494 0.2537 0.2518 0.2564 0.2603 0.2683 0.2530 0.5006 0.5027	74.4 74.8 70.8 70.3 71.3 71.6 71.3 74.6 78.0 77.9	25 25 25 25 25 25 25 25 25 25 25 25 25 2	Hübl	17 hours
12 13 14 15	I I H I	0.1013 0.1036 0.2464 0.6451	81.1 79.3 74.0 71.4	25 25 25 50	Hanus	30 min- utes
16 17 18 19 20 21	D D D D D	0.1269 0.2501 0.2516 0.2506 0.2529 0.5006 0.5036	144.7 106.0 100.3 154.2 158.9 56.4 55.1	25 25 25 50 50 25 25	Wijs	30 min- utes

The iodine number of cholesterol is 65.7. This figure is based on the formula  $C_{27}H_{46}O$ , the presence of one double bond in the molecule, and the atomic weights H=1.008; C=12.00; O=16.00; I=126.92. The values obtained in this research are all higher than the theoretical value, save in experiments 21 and 22 by the Wijs method. The Hübl method tended to give

Vol. CLXXVI, No. 1054-31

the lowest values; although even in experiments 10 and 11, where the conditions were as prescribed by Lewkowitsch 14 (0.5 to 0.6 gramme cholesterol, 50 c.c. chloroform, and 25 c.c. of each solution or 50 c.c. of the mixed reagent of Hübl), the iodine number is too high. In the Hanus method the tendency is toward still higher results, while the highest values of all are obtained by the use of the Wijs method. Thus the iodine numbers obtained in experiments 16, 19, and 20 are over twice the theoretical value. There is a marked tendency, especially apparent in the case of the Hanus and Wijs methods, for the iodine number to become higher, the greater the excess of the iodine reagent. These phenomena might be explained by the saturation of a second double bond or, possibly, by the breaking of an intracyclic bond or bridge; however, in such a case the iodine number would be a simple multiple of 65.7, and the results obtained are not simple multiples of that figure. The explanation of these results must therefore be sought in another direction—possibly saturation of the one double bond is followed by direct substitution of halogen. The iodine numbers here obtained demonstrate that cholesterol cannot be determined volumetrically by means of the iodine reagents of fat analysis.

## IV. METHODS FOR THE QUANTITATIVE DETER-MINATION OF CHOLESTEROL.

GRAVIMETRIC DETERMINATION AS FREE CHOLESTEROL.

In the gravimetric methods for the quantitative determination of cholesterol the latter is weighed as the free alcohol, as cholesteryl benzoate or as digitonin cholesteride. Ritter <sup>91</sup> has made an exhaustive study of the extraction and determination, gravimetrically, of cholesterol as the free alcohol. He recommends that 50 grammes of fat be dissolved in 100 c.c. of boiling alcohol in a porcelain dish of 1500 c.c. capacity; 8 grammes of metallic sodium are dissolved in 160 c.c. of 99 per cent. alcohol, and the hot solution of sodium ethylate is immediately added to the boiling alcoholic solution of the fat; the mixture is well stirred and is evaporated until the alcohol has been completely removed. Sodium chloride, in weight one and one-half times that of the fat, is added, and, in order to insure an intimate mixture of the soaps and salt, the latter are almost, if not entirely, dissolved in

water. The solution is evaporated with frequent stirring, over a free flame, until crystallization begins, then on the water-bath until dry. The dish and its contents are then further dried in an oven at 80° C., and the process of pulverizing the residue in the dish is begun as soon as the latter is sufficiently dry. A fine powder is finally obtained, which is dried in a desiccator over sulphuric acid, then is extracted with ether in a Soxhlet apparatus for a period of nine hours. The ether extract is then poured into an Erlenmeyer flask of 750 to 1000 c.c. capacity, and the extraction flask is washed with several successive portions of ether, which are also poured into the Erlenmeyer flask. The ether is evaporated; the residue is dissolved in a very small quantity of alcohol on the water-bath, and water is gradually added, agitating the flask meanwhile, until it is almost full. The precipitated cholesterol is collected on a filter and washed with water. The filter and its contents are dried at 60° C., the cholesterol is transferred, as far as possible, to a tared flask; the filter is washed with ether to remove the last traces of cholesterol, and these washings are received in the tared flask. The ether is evaporated, and the residue is completely dried at 100-120° C., then weighed. According to Ritter, the sodium chloride gives porosity to the dry mass, prevents the solution of the soaps in ether, and also has another specific action in assisting the solution of the cholesterol in the ether. The nature of this specific action, which is not exerted by sand or paper, Ritter states cannot be explained with certainty. Corper 92 found that the presence of an excess of sodium ethylate in the mixture of soaps and salt prevents the quantitative extraction of the cholesterol by the ether. In a second paper Corper 93 states that this error may be eliminated by passing a current of carbon dioxide gas through the aqueous solution of the soaps for a period of three to five hours in order to decompose the excess of ethylate. The salt is then added and the procedure carried out as outlined above.

Cappenberg 94 has devised the following method for the isolation and gravimetric determination of cholesterol as the free alcohol. The ether extract of the crude material is saponified with alcoholic potash, the soap solution is evaporated to complete dryness, and the residue is ground and extracted with absolute ether. The ethereal solution is filtered; the ether is

evaporated and the residue is dissolved in hot methyl alcohol. Twenty per cent. of water is added to the hot solution, which is then concentrated until crystallization of the cholesterol begins. The solution is then cooled to 0° C., whereupon all the cholesterol separates as crystals, which are at once collected on a tared filter and washed first with 50 per cent. methyl alcohol, then with hot water. The filter and its contents are dried at 100° C. to constant weight.

Usually cholesterol is determined in a fat or in the ether extract of a tissue, excrement, or food. Grigaut 95 uses tissue itself. He directs that 20 to 40 c.c. of blood-serum or 2 to 10 grammes of freshly-ground tissue be mixed with 60 to 80 c.c. of a 20 per cent. aqueous soda solution in a flask, which is closed with a cotton plug. The flask and its contents are heated for one hour at 110° C. in an autoclave. After cooling, the aqueous solution is transferred to a separatory funnel and shaken with one or two volumes of common ether. The extraction with ether is repeated, the two ether extracts are combined, and the solvent is evaporated. The residue is dissolved in a small quantity of alcohol; I c.c. of alcoholic soda is added; the solution is evaporated to dryness, and the residue is kept in an oven at 100° C. for 30 minutes. While the dish is still warm, the residue is dissolved in petroleum ether; the solution is filtered and the filter is washed with petroleum ether. The combined filtrate and washings are evaporated, and the residue of cholesterol is dried at 100° C. to constant weight.

#### GRAVIMETRIC DETERMINATION AS CHOLESTERYL BENZOATE.

The gravimetric determination of cholesterol as cholesteryl benzoate has been described by Dorée and Gardner<sup>20</sup>. They direct that I gramme of the unsaponifiable portion of the ether extract be dissolved in 10 to 20 c.c. of pyridine. A slight excess of benzoyl chloride, dissolved in pyridine, is added, and the solution is allowed to stand for several hours, then poured into water. The precipitated cholesteryl benzoate is recrystallized from absolute alcohol. According to Gardner,<sup>96</sup> at 20° C. each 100 c.c. of the mother liquor retains 0.12 gramme of the ester. The crystals are more difficultly soluble; after standing in alcohol for several hours at 20° C., with occasional shaking, only 0.029 gramme of the crystalline benzoate had dissolved in each 100 c.c. of solvent.

#### GRAVIMETRIC DETERMINATION AS DIGITONIN CHOLESTERIDE.

The preceding methods have been available for the determination of total cholesterol only. The digitonin cholesteride method of Windaus<sup>62</sup> permits the determination of free, esterified, and total cholesterol. Free cholesterol combines with the glucoside digitonin (digitin, digitalin) to form digitonin cholesteride. One molecule of cholesterol C<sub>27</sub>H<sub>46</sub>O unites with one molecule of digitonin C55H94O28 without elimination of water to form the cholesteride  $C_{82}H_{140}O_{29}$ . The cholesterol should be dissolved in fifty-fold its quantity of boiling 95 per cent. alcohol; the digitonin should be a I per cent. solution in hot 90 per cent. alcohol; when the hot solutions are mixed, the digitonin cholesteride is precipitated. The weight of the cholesteride, after drving at 100° C., is multiplied by the factor 0.2431 in order to obtain the weight of cholesterol contained in it. The esters of cholesterol do not react with digitonin, but remain in solution. Windaus studied the cholesterol content of kidneys. The ether extract of these organs was treated with thirty-fold its quantity of boiling 95 per cent. alcohol. Whenever the extract was not completely soluble in the alcohol, it was boiled with several successive portions of that solvent in order to completely remove free cholesterol, which was then determined in the combined alcoholic solutions. The solution of digitonin was added as long as a precipitate formed. After having stood for several hours in order to permit the precipitate to settle, the supernatant liquid was tested with digitonin solution to make sure that all the free cholesterol had been precipitated. The precipitate was collected on a Gooch crucible, washed with alcohol and ether, dried at 100° C., and weighed. The quantity of free cholesterol was then calculated.

That portion of the original ether extract of the kidney which was insoluble in alcohol was dissolved in a mixture of alcohol and ether, and was combined with the filtrate and washings from the determination of free cholesterol. The alcoholether solution was concentrated, diluted with water, and extracted with ether or petroleum ether, which dissolved out the lipins, including the cholesteryl esters. The ether was evaporated; the residue was saponified by means of hot sodium ethylate in order to liberate the cholesterol from its esters; the

cholesterol was extracted from the solution with petroleum ether, and was finally precipitated and weighed as digitonin cholesteride. The quantity of esterified cholesterol was then calculated. The total cholesterol was the sum of the free and esterified cholesterol.

#### VOLUMETRIC METHODS.

The volumetric methods which have been suggested for the determination of cholesterol are:

- (a) Determination of the iodine number.
- (b) Determination of the acetyl saponification number.
- (c) Titration with bromine.

Lewkowitsch <sup>14</sup> recommended the use of the iodine number, as determined by Hübl's method, for the volumetric estimation of cholesterol. However, since the iodine number of cholesterol varies between wide limits and is always abnormally high, as was shown in Part III of this dissertation, this method is not quantitative.

Lewkowitsch <sup>14</sup> by experiment obtained 137.4 and 132.4 as the acetyl saponification number of cholesterol (the saponification number of cholesteryl acetate), while the theoretic value was 135.5. He therefore recommended the determination of this constant as an admirable method for the estimation of cholesterol, as such, in mixtures with other lipins which do not influence the reaction.

According to Nukada,<sup>97</sup> the true acetyl value (which is a measure of hydroxyl groups) of the fat of man, swine, sheep, geese, and of their insoluble fatty acids, cannot be taken as a measure of the quantity of free and total cholesterol respectively, for the values are far too high to check with determinations of unsaponifiable matter, and are influenced by the hydroxy acids of the fat.

Obermüller <sup>98</sup> determined the cholesterol content of the unsaponifiable matter of a fat or oil by titration with bromine. The unsaponifiable matter was dissolved in a few cubic centimetres of carbon disulphide, and a 2.97 per cent. solution of bromine in carbon disulphide was added from a burette until a distinct change in color from yellow to yellowish-red occurred. Therefore cannot be used as the solvent.

#### COLORIMETRIC METHODS.

The methods for the colorimetric determination of cholesterol are based on the reactions of Salkowski 99 and Liebermann. 100 Schulze 101 has used these reactions in the colorimetric determination of phytosterol. The colorimetric determination of total cholesterol by means of Liebermann's reaction has been studied by Grigaut. 102 He recommends that 2 c.c. of blood-serum or 0.1 to 1.0 gramme of freshly-ground tissue be heated on a water-bath for 5 to 20 minutes with 20 c.c. of I per cent. solution of soda in 50 per cent. alcohol. After cooling, the solution is extracted, first with 50 c.c. of ether, then with 30 c.c. of the same solvent. The combined ether extracts are washed with water; the ether is evaporated; the residue is dissolved in 5 c.c. of chloroform; 2 c.c. of pure acetic anhydride are added, followed by 2 drops of concentrated sulphuric acid. The color is permitted to develop. In one-half hour it passes through red, blue, bluish-green, to a beautiful green, which persists for one hour. At the same time, a standard is prepared by treating 5 c.c. of a solution of 0.06 gramme of cholesterol in 100 c.c. of chloroform with acetic anhydride and concentrated sulphuric acid as just described. Should the color of the standard not match that of the determination proper, the more intensely colored solution is diluted with a mixture of chloroform, acetic anhydride, and concentrated sulphuric acid, which contains these reagents in the proportions already indicated, until the colors are of the same intensity. The quantity of cholesterol in the unknown is then calculated. The results obtained by this colorimetric method may differ by one-fifteenth from the results obtained by Grigaut's gravimetric method,95 which gives the higher figures.

Weston 103 and Weston and Kent 37 have applied the Sal-kowski reaction for the colorimetric determination of total cholesterol in blood analysis. According to these investigators, the presence of less than two milligrammes of cholesterol in one cubic centimetre of chloroform gives rise to the following phenomena in Salkowski's reaction. Both the chloroform solution and the sulphuric acid rapidly pass through a yellowish-green to an amber color, which remains unchanged for about an hour, then becomes pink, and finally violet. However, after the

mixture has stood for 15 to 30 minutes, the addition of a small quantity of chloroform causes the amber color to disappear, and, in a few minutes, the colorless solution begins to show the pink tint which is characteristic of cholesterol. The crude cholesterol, obtained from 2.5 c.c. of serum as described below, is dissolved in 5 c.c. of chloroform, and 0.15, 0.2 and 0.25 c.c. of this solution are diluted to a volume of I c.c. each with chloroform. Nine standard solutions of cholesterol are prepared by diluting with chloroform a solution of 0.5 gramme of cholesterol in 50 c.c. of that solvent, so that I c.c. of the standards represents 0.0001. 0.000125, 0.00015, 0.000175, 0.0002, 0.000225, 0.00025, 0.000275, and 0.0003 gramme of cholesterol, respectively. One cubic centimetre of each dilution of the unknown and of each standard is placed in a separate tube, the dimensions of which are I cm. by 10 cm.; 0.1 c.c. of sulphuric acid (1.81 sp. gr.) is added to each tube, which is then shaken twenty times and permitted to stand for 30 minutes. At the end of that period of time, I c.c. of chloroform is added to each tube without disturbing the sulphuric acid. The tubes are placed in the dark for 15 minutes. As soon as the series of standards shows a gradation of color from barely perceptible pink to deep pink, they are compared with the unknowns and the cholesterol content of the latter is calculated. The comparison is made by looking through the tubes, while holding them against a white surface. color of the unknown should lie near or slightly below the middle of the scale of standards. The chloroform used must be of a high degree of purity. The extraction of the crude cholesterol from serum may be outlined. The 2.5 c.c. of serum are treated successively with alcohol at 60 ° C., ether, and boiling alcohol. The alcohol and ether solutions are combined and saponified with sodium hydroxide, then treated with calcium hydroxide solution, which produces a precipitate containing all the cholesterol. The dried precipitate is extracted with several portions of ether in order to recover the cholesterol; the ether is evaporated and the residue is used for the colorimetric estimation of cholesterol.

### STUDY OF THE GRAVIMETRIC METHODS.

In the following experiments the gravimetric determination of cholesterol as the free alcohol, as cholesteryl benzoate, and as digitonin cholesteride was studied.

## Determination of Cholesterol as the Free Alcohol.

Cappenberg's Method (Table VI).—In order to learn the influence of the crystallization from methyl alcohol on the quantitative yield of cholesterol, experiments 23 and 24 were carried out. The cholesterol was dissolved in 15 c.c. of hot methyl alcohol; the solution was concentrated to a volume of 10 c.c., and 2 c.c. (20 per cent.) of water were added, whereupon crystals of cholesterol separated. The solution was permitted to cool to the temperature of the room, and was further cooled by packing in ice and salt for a period of five to fifteen minutes. The cold supernatant liquid was poured into a tared Gooch crucible: the precipitate of cholesterol was transferred to the crucible, and was washed with 20 c.c. of ice-cold 50 per cent. methyl alcohol, then with 50 to 75 c.c. of hot water. The crucible and its contents were dried for two hours at 100-110 ° C., permitted to cool in a desiccator over calcium chloride, and weighed. The filtrate and the alcoholic washings were perfectly clear, but the dilution with the aqueous washings gave rise to a slight opales-The results show that a loss of cholesterol occurred during the crystallization.

TABLE VI.

DETERMINATION OF CHOLESTEROL BY THE METHOD OF CAPPENBERG.

Experiment number	Sample	Weight of choles- terol taken	Weight of choles- terol found	Per cent. of cho- lesterol recovered
23	H	0.2089	0.2049	98.09
24	H	0.2010	0.1982	98.61
25	H	0.2099	0.1983	94.47
26	H	0.2042	0.1927	94.37

The complete procedure of Cappenberg was carried out in experiments 25 and 26. The cholesterol was heated on the water-bath for thirty minutes with 50 c.c. of alcoholic potash, and the solution was then evaporated to complete dryness. The residue was ground and extracted with absolute ether; the ethereal solution was filtered; the filter was washed with ether, and the combined filtrate and washings were evaporated to dryness on the water-bath. The residue of cholesterol was subjected to crystallization from methyl alcohol, as was described in detail

for the preceding set of experiments. The dilute methyl alcohol and the water which were used for washing the cholesterol ran through the Gooch crucible rather slowly.

When the results of the two sets of experiments were compared it was seen that, during the complete procedure of saponification, extraction and crystallization (experiments 25 and 26), a greater loss of cholesterol occurs than takes place during the process of crystallization alone (experiments 23 and 24).

Ritter's Method (Table VII).—Two experiments (27 and 28) were carried out as directed by Corper. 93 The cholesterol was dissolved in 10 c.c. of absolute alcohol—in a large beaker with the aid of heat. Forty cubic centimetres of an alcoholic solution of sodium ethylate (5 grammes of sodium dissolved in 100 c.c. of absolute alcohol) were added, and the solution was heated on a water-bath for twenty minutes, then permitted to stand over night. One hundred cubic centimetres of water were added, and a slow current of carbon dioxide was passed for five consecutive hours through the resulting suspension of cholesterol. The gas was generated in a Kipp apparatus by the action of hydrochloric acid on marble, and was washed by passing through a solution of sodium bicarbonate. The suspension was heated and transferred quantitatively to a casserole; 30 grammes of sodium chloride were added and the solution was evaporated to complete dryness by prolonged heating on the water-bath. was ground in a mortar, transferred to a fat-free paper thimble, dried in the oven at 100-110° C., and extracted for nine hours with absolute ether in a Soxhlet extractor.

The ether was transferred to a separatory funnel; the extraction flask was washed several times with ether and the washings were added to the ethereal extract. The ethereal solution was washed three times with water, then transferred to a small tared flask. The combined wash waters were shaken with ether to recover any cholesterol in them; the ether was washed twice with water, and then transferred to the tared flask containing the ethereal solution. The ether was evaporated on the water-bath and the flask was dried for two hours at 100–110° C. and weighed. Corper states that this method is "accurate within milligrammes."

The treatment with carbon dioxide requires several hours. In order to shorten the period of time required for the neutraliza-

tion of the excess of sodium ethylate, three experiments—29 to 31, inclusive—were carried out as outlined above, but, instead of treatment with carbon dioxide, the aqueous-alcoholic suspension of cholesterol was neutralized with 2/N hydrochloric acid solution, using phenolphthalein as the indicator. In addition to the sodium chloride, 2 grammes of sodium bicarbonate were added in order to insure the presence of sodium carbonate in the dried residue after evaporation.

When carbon dioxide was used, good duplicates were not obtained, although the cholesterol used in the two experiments was from the same source and had the same melting-point. When hydrochloric acid was used, two of the results were excellent duplicates, but the third result was far too low. The values obtained after the use of hydrochloric acid are lower than those obtained after the use of carbon dioxide. The method, on the whole, tends to give lower results than does the method of Cappenberg.

TABLE VII.

DETERMINATION OF CHOLESTEROL BY MODIFICATIONS OF RITTER'S METHOD.

Experi- ment number	Sample	Weight of choles- terol taken	Weight of choles- terol found	Per cent. of cholesterol	Acid used for neutralization
27 28 29 30 31	H I H H	0.1038 0.1043 0.1046 0.1037 0.1018	0.1037 0.0964 0.0673 0.0924 0.0907	99.90 } 92.43 } 64.34 } 89.10 }	Carbon dioxide Hydrochloric acid

## Determination of Cholesterol as Cholesterol Benzoate.

The cholesterol was dissolved in 5 to 10 c.c. of pyridine, and a solution of 0.5 c.c. of benzoyl chloride in 5 c.c. of pyridine was added. The resulting solution was well mixed and permitted to stand over night at the temperature of the room, then was poured into water. In experiments 32 to 35, inclusive, 80 to 100 c.c. of water were used; in experiments 36 to 38, inclusive, 500 c.c. of water were used. On stirring, a white flocculent precipitate of cholesteryl benzoate separated, which at first floated, then settled to the bottom of the beaker. The supernatant liquid was somewhat opalescent. The precipitate was collected on a

smooth, hardened filter-paper; the filtrate was perfectly clear, and its chloroform extract gave a negative reaction with Salkowski's reagent, hence contained no cholesterol. The precipitate was washed with a few cubic centimetres—5 to 7—of cold alcohol, and was then recrystallized from alcohol.

The directions of Gardner <sup>96</sup> are rather indefinite as to the strength of the alcohol to be used for this purpose. He states that cholesteryl benzoate "is only slightly soluble in absolute alcohol. If recrystallized from alcohol, the mother liquors retain at 20° 0.12 gramme per 100 c.c. The crystals are, however, more difficultly soluble. The writer found that on allowing crystals to stand in alcohol at 20° for several hours with occasional shaking only 0.029 gramme dissolved in 100 c.c." He also directs that the recrystallized cholesteryl benzoate be weighed, "in which case a correction may be made for the solubility in alcohol."

Absolute alcohol was used throughout experiments 32 to 36, inclusive; 95 per cent. alcohol was used in experiments 37 and 38. The filter and precipitate were boiled with several successive portions of alcohol, the hot solution of cholesteryl benzoate was filtered, and the filter washed with hot alcohol. The combined filtrate and washings were concentrated to a volume of approximately 20 c.c., then permitted to stand over night at the temperature of the room. The precipitate of cholesteryl benzoate was collected on a tared Gooch crucible and sucked free from mother liquor, the volume of which was then measured. The precipitate was next washed with a known volume of alcohol, dried for two hours at 100–110° C., and weighed.

Table VIII presents data for the volume of mother liquor, the cholesteryl benzoate content of which has been calculated in grammes by multiplying the volume in cubic centimetres by the factor 0.0012. In that table the volume of wash alcohol is also given; its content of cholesteryl benzoate in grammes has been obtained by multiplying the volume in cubic centimetres by the factor 0.00029. The sum of the weight of crystalline cholesteryl benzoate plus that of the ester contained in the mother liquor and in the washings is the "Total weight of cholesteryl benzoate," from which the corresponding weight of cholesterol has been calculated.

When 95 per cent. alcohol was used for recrystallization

TABLE VIII.

Determination of Cholesterol as Cholesteryl Benzoate.

1	1						
Per cent. of cholesterol recovered	43.45	30.26	30.41	24.29	50.41	61.79	59.41
Weight of cholesterol corresponding to weight of total benzoate	0.2224	0.1536	0.1523	0.1257	0.2592	0.3137	0.3006
Total weight of cholesteryl benzoate	0.2823	0.1950	0.1933	0.1596	0.3290	0.3982	0.3816
Weight of cholesteryl benzoate in wash alcohol	0.0058	0.0058	0.0058	0.0058	0.0058	0.0073	0,0080
Weight of cholesteryl benzoate in mother liquor	0.0174	0.0224	0.0130	0.0128	0.0154	0.0186	0.0233
Volume of wash alcohol, c.c.	20.0	20.0	20.0	20.0	20.0	25.2	27.6
Volume of mother liquor, c.c.	14.5	18.7	10.8	7.01	12.8	15.5	19.4
Weight of cholesteryl benzo- ate crystals	0.2591	0,1668	0.1745	0.1410	0.3078	0.3723	0.3503
Weight of cholesterol taken	0.5119	0.5076	0.5008	0.5174	0.5142	0.5077	0.5060
Sample	Н	H	н	Н	H	Q	D
Experiment number	32	33	34	35	36	37	38

(experiments 37 and 38), the per cent. of cholesterol recovered was somewhat higher than in any of the other experiments, where absolute alcohol was used. However, in no case was even two-thirds of the weight of cholesterol taken recovered. The least amount recovered was 24.29 per cent., the greatest 61.79 per cent., the average of the seven experiments 42.86 per cent. This method, therefore, is not quantitative. Since no cholesterol was present in the aqueous filtrate from the precipitate of cholesteryl benzoate, and since that precipitate was completely dissolved in the boiling alcohol, the cholesterol not recovered must have remained in the alcoholic mother liquors, and the solubility of cholesteryl benzoate in alcohol must be greater than the values recorded in the literature. However, since from one-third to three-fourths of the cholesterol taken was not recovered, a redetermination of the solubility of the ester in alcohol and new correction factors based thereon would not render the determination of cholesterol as cholesteryl benzoate a suitable method for gravimetric analysis.

## Determination of Cholesterol as Digitonin Cholesteride.

The cholesterol was dissolved in 10 c.c. of 95 per cent. alcohol; to this boiling solution was added an excess of a boiling I per cent. solution of digitonin in 90 per cent. alcohol. One part by weight of cholesterol combines with slightly more than three parts by weight of digitonin. In order to insure the presence of an excess of the latter, four parts by weight of digitonin were always used for one part by weight of cholesterol. After the two boiling solutions had been mixed, the resulting mixture was permitted to stand over night at room temperature. Precipitation of digitonin cholesteride usually began in the boiling solution and was completed on standing. The precipitate was collected on a tared Gooch crucible, washed with 95 per cent. alcohol and ether, dried for two hours at 100-110° C., and weighed. The cholesterol content of the precipitate was calculated by multiplying the weight of the latter by the factor 0.2431. The filtrate and washings ran through the Gooch crucible rather slowly. When the digitonin was dissolved in absolute alcohol, it produced no precipitate in solutions of cholesterol in 95 per cent, alcohol; however, after sufficient water had been added to the mixture to reduce the strength of the alcohol derived from

the digitonin solution to 90 per cent., the precipitate formed quantitatively.

The results obtained by this method are given in Table IX. The least proportion of cholesterol recovered was 93.63 per cent., the greatest 103.02 per cent.; the average of ten experiments was 97.37 per cent.

TABLE IX.

DETERMINATION OF CHOLESTERIOE. AS DIGITORIN CHOLESTERIDE.

Experi- ment number	Sample	Weight of choles- terol taken	Weight of digitonin cholesteride	Weight of choles- terol found	Per cent. of cholesterol recovered
39	A B C D E F I I I I I	0.0511	0.2039	0.0496	97.06
40		0.0501	0.1995	0.0485	96.81
41		0.0511	0.2081	0.0506	99.02
42		0.0496	0.2101	0.0511	103.02
43		0.0502	0.1932	0.0470	93.63
44		0.0523	0.2168	0.0527	100.76
45		0.0498	0.1953	0.0475	95.38
46		0.0512	0.2022	0.0492	96.09
47		0.1468	0.5787	0.1407	95.84
48		0.1521	0.6015	0.1462	96.12

# Comparison of the Grazimetric Methods.

The gravimetric determination of cholesterol as the free alcohol, as cholesteryl benzoate, and as digitonin cholesteride has been studied in the course of this research.

Of the methods for the determination as the free alcohol, that of Cappenberg (Table VI) is preferable to the modified Ritter method (Table VII). By Cappenberg's procedure excellent duplicates were obtained; while in the Ritter methods unsatisfactory duplicates were the rule when carbon dioxide was used, and the results were too low when hydrochloric acid was used.

The determination of cholesterol as cholesteryl benzoate (Table VIII) is not a quantitative method.

The determination of cholesterol as digitonin cholesteride (Table IX) is the best method of all. It is the most accurate, surpassing even Cappenberg's method in this respect, and, moreover, is by far neater and less complicated than the latter.

# V. CONCLUSIONS.

Cholesterol, extracted from brain, has been purified by saponification either with sodium ethylate at room temperature or with

boiling alcoholic potash, in each case followed by crystallization from ether. Cholesterol has also been prepared from gall-stones by extraction with ether and crystallization from that solvent.

The melting-points of the six samples from brain, 148.4–149.1° C.; of the two samples from gall-stones, 147.4° C., and of various mixtures of two samples (50 per cent. of each sample), 147.7–148.0° C., demonstrate the identity of the cholesterol from the two sources.

The melting-points of the samples and of their mixtures also show that neither heat in the process of saponification, nor alkaline reagents such as alcoholic potash and sodium ethylate, produce any rearrangement in the molecule of cholesterol.

The iodine reagents of fat analysis cannot be used for the volumetric determination of cholesterol. The iodine number of pure cholesterol has been determined by the methods of Hübl, Hanus, and Wijs. The Hübl method tended to give the lowest values, 70.3–78.0, but even these values were higher than the theoretic value 65.7, which is based on the presence of one double bond in the molecule of cholesterol. The Hanus method gave still higher results, 71.4–81.1, while the highest values of all were obtained by the Wijs method, 55.1–158.9, with a tendency to lie above 100. There was a marked tendency, especially in the Hanus and Wijs methods, for the iodine number to become higher, the greater the excess of the iodine reagent. However, the iodine numbers were not simple multiples of 65.7, hence the presence of a second double bond in cholesterol is doubtful.

The gravimetric determination of cholesterol as the free alcohol by modifications of Ritter's method is unsatisfactory. When carbon dioxide was used to neutralize the excess of sodium ethylate, divergent duplicates were obtained, 99.90 and 92.43 per cent. of the cholesterol taken being recovered. When hydrochloric acid was used to neutralize the excess of sodium ethylate, the results were still less satisfactory, 64.34–89.10 per cent. of the cholesterol taken being recovered.

The gravimetric determination of cholesterol as the free alcohol by Cappenberg's method gave excellent duplicates; 94.47 and 94.37 per cent. of the cholesterol taken was recovered.

The gravimetric determination of cholesterol as cholesteryl

benzoate is not quantitative, but 24.29 to 61.79—average 42.86 per cent. of the cholesterol taken—was recovered.

The gravimetric determination of cholesterol as digitonin cholesteride was the most accurate and most satisfactory of the methods studied. From 93.63 to 103.02—average 97.37 per cent. of the cholesterol taken—was recovered.

#### ACKNOWLEDGMENT.

This research was undertaken at the suggestion of Prof. William J. Gies, and was carried out under his guidance. The author wishes gratefully to record his deep indebtedness for the encouragement, kindly criticism, and helpful suggestions which have been freely bestowed upon him by Dr. Gies during the progress of the investigation.

Laboratory of Biological Chemistry of Columbia University in the City of New York
At the College of Physicians and Surgeons,
1913.

### BIBLIOGRAPHY.

- 1 Chevreul, Annaies de Chimie, 1815, xcv, 7.
- <sup>a</sup> Berthelot, Annales de Chimie et de Physique, 1859, (III), lvi, 51.
- <sup>3</sup> Planer, Annalen der Chemie und Pharmacie, 1861, cxviii, 25.
- <sup>4</sup> Diels and Abderhalden, Berichte der deutschen chemischen Gesellschaft, 1904, xxxvii, 3092.
- <sup>5</sup> Lindenmeyer, Journal für praktische Chemie, 1863, xc, 321. <sup>6</sup> Obermüller, Zeitschrift für physiologische Chemie, 1891, xv, 37.
- Walitzky, Berichte der deutschen chemischen Gesellschaft, 1878, xi, 1937.
- Bloch, Bulletin de la Société chimique de Paris, 1904, (III), xxxi, 71.
- <sup>9</sup> Mauthner and Suida, Monatshefte für Chemie, 1896, xvii, 29.
- 10 Windaus, Berichte der deutschen chemischen Gesellschaft, 1906, xxxix, 2008.
- <sup>11</sup> Dorée and Gardner, Journal of the Chemical Society, Transactions, 1908, xciii, 1328.
- <sup>12</sup> Wislicenus and Moldenhauer, Annalen der Chemie und Pharmacie, 1868, cxlvi, 175.
- <sup>13</sup> Mauthner and Suida, Monatshefte für Chemie, 1894, xv, 85.
- 14 Lewkowitsch, Berichte der deutschen chemischen Gesellschaft, 1892, xxv, 65.
- 15 Mauthner, Monatshefte für Chemie, 1906, xxvii, 305.
- <sup>16</sup> Willstätter and Mayer, Berichte der deutschen chemischen Gesellschaft, 1908, xli, 2199.
- Molinari and Fenaroli, Berichte der deutschen chemischen Gesellschaft, 1908, xli, 2785.

Vol. CLXXVI, No. 1054-32

- <sup>18</sup> Mauthner and Suida, Monatshefte für Chemie, 1894, xv, 362.
- Windaus, "Abderhalden's Biochemisches Handlexikon," 1911, III, 268; Archiv der Pharmazie, 1908, ccxlvi, 117; Berichte der deutschen chemischen Gesellschaft, 1908, xli, 2558.
- <sup>20</sup> Dorée and Gardner, Proceedings of the Royal Society of London, 1908, B, lxxx, 227.
- <sup>21</sup> Bömer, Zeitschrift für Untersuchung der Nahrungs- und Genussmittel, 1901, iv, 1070.
- <sup>22</sup> Schultz, Biochemische Zeitschrift, 1912, xlii, 255.
- <sup>23</sup> Brücke, Zeitschrift für analytische Chemie, 1862, i, 257.
- <sup>24</sup> Pennington and Robertson, United States Department of Agriculture, Bureau of Chemistry Circular 104, 1912.
- <sup>25</sup> Glikin, Biochemisches Centralblatt, 1908, vii, 289, 357.
- 20 Porges and Neubauer, Biochemische Zeitschrift, 1908, vii, 152.
- <sup>27</sup> Porges and Neubauer, Zeitschrift für Chemie und Industrie der Kolloide, 1909, v, 193.
- \* Loewe, Biochemische Zeitschrift, 1912, xlii, 207.
- 29 Gies, Biochemical Bulletin, 1912, ii, 55.
- 30 Rosenbloom, Biochemical Bulletin, 1912, ii, 64.
- 31 Windaus, Berichte der deutschen chemischen Gesellschaft, 1909, xlii, 238.
- 82 Pringsheim, Münchener medizinische Wochenschrift, 1912, lix, 1757.
- 33 Richter, Therapeutische Monatshefte, 1908, xxii, 590.
- <sup>34</sup> Robertson and Burnett, Proceedings of the Society for Experimental Biology and Medicine, 1912, x, 59.
- <sup>16</sup> Desmoulière, Comptes rendus des séances de l'Académie des Sciences, 1912, clv, 592, 927, 1110.
- <sup>56</sup> Grimbert and Laudat, Comptes rendus des séances de l' Académie des Sciences, 1912, clv, 974.
- <sup>87</sup> Weston and Kent, Journal of Medical Research, 1912, xxvi (New Series xxi), 531.
- 88 Hermann and Neumann, Biochemische Zeitschrift, 1912, xliii, 47.
- 30 Dorée, Bio-Chemical Journal, 1909, iv, 72.
- \*OVirchow, Zeitschrift für Untersuchung der Nahrungs- und Genussmittel, 1899, ii, 559.
- König and Schluckebier, Zeitschrift für Untersuchung der Nahrungs- und Genussmittel, 1908, xv, 641.
- <sup>42</sup> Fraser and Gardner, Proceedings of the Royal Society of London, 1910, B, lxxxii, 559.
- 43 Flint, American Journal of the Medical Sciences, 1862, New Series xliv,
- "von Bondzynski and Humnicki, Zeitschrift für physiologische Chemie, 1896-7, xxii, 396.
- 45 von Bondzynski, Berichte der deutschen chemischen Gesellschaft, 1896, xxix, 476.
- 46 Flint, Zeitschrift für physiologische Chemie, 1897, xxiii, 363.
- 47 Müller, Zeitschrift für physiologische Chemie, 1900, xxix, 129.
- <sup>48</sup> Dorée and Gardner, Proceedings of the Royal Society of London, 1908, B, lxxx, 212.

- 40 Kusumoto, Biochemische Zeitschrift, 1908, xiv, 416.
- 60 Kusumoto, Biochemische Zeitschrift, 1908, xiv, 411.
- <sup>61</sup> Ellis and Gardner, Proceedings of the Royal Society of London, 1909, B, lxxxi, 505.
- <sup>52</sup> Jankau, Archiv für experimentelle Pathologie und Pharmakologie, 1892, xxix, 237.
- <sup>58</sup> Goodman, Hofmeister's Beiträge zur chemischen Physiologie und Pathologie, 1907, ix, 91.
- 54 Pribram, Biochemische Zeitschrift, 1906, i, 413.
- <sup>65</sup> Dorée and Gardner, Proceedings of the Royal Society of London, 1909, B, lxxxi, 109.
- 56 Stadelmann, Zeitschrift für Biologie, 1896, xxxiv (N. F. xvi), 1.
- <sup>51</sup> Fraser and Gardner, Proceedings of the Royal Society of London, 1909, B, lxxxi, 230.
- 68 Ellis and Gardner, Proceedings of the Royal Society of London, 1912, B, lxxxiv, 461.
- Ellis and Gardner, Proceedings of the Royal Society of London, 1912, B, lxxxv, 385.
- <sup>60</sup> Ellis and Gardner, Proceedings of the Royal Society of London, 1909, B, lxxxi, 129.
- a Corper, Journal of Biological Chemistry, 1912, xi, 44.
- Windaus, Zeitschrift für physiologische Chemie, 1910, lxv, 110.
- <sup>43</sup> Duranton, La Cholestérine et ses Conditions de Précipitation. Thése pour le Doctorat en Médecine, Faculté de Médecine de Paris, 1908.
- 64 Kusumoto, Biochemische Zeitschrift, 1908, xiii, 354.
- 65 Kusumoto, Biochemische Zeitschrift, 1908, xiv, 407.
- \*Lifschütz, Zeitschrift für physiologische Chemie, 1906-7, 1, 436.
- or Lifschütz, Berichte der deutschen chemischen Gesellschaft, 1908, xli, 252.
- <sup>68</sup> Lifschütz, Zeitschrift für physiologische Chemie, 1907, liii, 140.
- \* Lifschütz, Zeitschrift für physiologische Chemie, 1908-9, lviii, 175.
- Rosenbloom and Gies, Biochemical Bulletin, 1911, i, 53.
- <sup>11</sup> Baumstark, Zeitschrift für physiologische Chemie, 1885, ix, 145.
- 12 Bünz, Zeitschrift für physiologische Chemie, 1905, xlvi, 47.
- <sup>13</sup> Rosenheim, Journal of Physiology, 1906, xxxiv, 104.
- 14 Tebb, Journal of Physiology, 1906, xxxiv, 106.
- 16 Frankel and Elfer, Biochemische Zeitschrift, 1912, xl, 138.
- <sup>76</sup> Rosenbloom, Journal of Biological Chemistry, 1913, xiv, 27.
- "Zuelzer, Zeitschrift für physiologische Chemie, 1899, xxvii, 255.
- <sup>18</sup> Koettstorfer, Zeitschrift für analytische Chemie, 1879, xviii, 199.
- <sup>19</sup> Kossel and Obermüller, Zeitschrift für physiologische Chemie, 1890, xiv, 599.
- Nossel and Krüger, Zeitschrift für physiologische Chemie, 1891, xv, 321.
- 81 Obermüller, Zeitschrift für physiologische Chemie, 1892, xvi, 152.
- <sup>82</sup> United States Department of Agriculture, Bureau of Chemistry, Bulletin 107 revised, 1908, 137.
- 83 Windaus, Chemiker Zeitung, 1906, xxx, 1011.
- <sup>84</sup> Marcusson, Chemiker Zeitung, 1907, xxxi, 419.
- \* Hübl, Dingler's Polytechnisches Journal, 1884, ccliii, 281.

- <sup>36</sup> Wijs (Wys), Berichte der deutschen chemischen Gesellschaft, 1898, xxxi, 750.
- 87 Hanus, Zeitschrift für Untersuchung der Nahrungs- und Genussmittel, 1901, iv, 913.
- 88 Waller, Chemiker Zeitung, 1895, xix, 1831.
- <sup>80</sup> United States Department of Agriculture, Bureau of Chemistry, Bulletin 107 revised, 1908, 136.
- Polenske, Quoted by Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 4th edition, 1000, i, 107.
- 91 Ritter, Zeitschrift für physiologische Chemie, 1901-2, xxxiv, 430.
- 92 Corper, Journal of Biological Chemistry, 1912, xi, 37.
- 93 Corper, Journal of Biological Chemistry, 1912, xii, 197.
- 94 Cappenberg, Chemiker Zeitung, 1909, xxxiii, 985.
- 95 Grigaut, Comptes rendus de la Société de Biologie, 1911, 1xxi, 441.
- <sup>96</sup> Gardner, "Allen's Commercial Organic Analysis," 4th edition, 1910, ii, 479.
- 97 Nukada, Biochemische Zeitschrift, 1908, xiv, 419.
- <sup>88</sup> Obermüller, Zeitschrift für physiologische Chemie, 1892, xvi, 143.
- Salkowski, Pflüger's Archiv für die gesammte Physiologie, 1872, vi, 207.
   Liebermann, Berichte der deutschen chemischen Gesellschaft, 1885, xviii, 1803.
- <sup>191</sup> Schulze, Zeitschrift für physiologische Chemie, 1890, xiv, 491.
- <sup>192</sup> Grigaut, Comptes rendus de la Société de Biologie, 1910, lxviii, 791, 827; 1911, lxxi, 513.
- 103 Weston, Journal of Medical Research, 1912, xxvi, (New Series xxi), 47.
- Hawk, "Practical Physiological Chemistry," 4th edition, 1913, 366.

Westphalian Coke Oven By-products. Anon. (Engineer, May 23, 1913.)—The coke produced in the Ruhr district, Rhenish Westphalia, in 1911, equalled the combined total output of British collieries and gas-works in the same year, and when the British figures for 1912 are available it will be found that the Westphalian pits alone have already surpassed them by many tons. As a result of the increased output of coke from the by-product ovens in the Ruhr, the production of gas and by-products has also expanded. The production of ammonium sulphate, which amounted to only 53,000 tons in Westphalia in 1903, had risen to 236,000 tons in 1911. During the same period the output of coal tar increased from 132,000 tons to 569,000 tons, while that of benzoline developed from 40,000 tons to 70,000 tons in 1911 and 84,000 tons in 1912, and will be further developed by the installation of new plants. The production of illuminating gas from the coke ovens advanced from 393,000 cubic metres in 1903 to 84,594,000 cubic metres in 1911, the gas being largely supplied to towns. Similarly, the output of electrical energy at the Ruhr pits has increased from 58,000,000 kilowatt-hours in 1906 to 592,000,000 kilowatt-hours in 1911, and further extensions were made in 1912. Most of the electrical energy is utilized for the collieries and the auxiliary plant, though the quantity sold to outside parties is continually increasing.

#### NOTES FROM THE U.S. BUREAU OF STANDARDS.\*

### THE LATENT HEAT OF FUSION OF ICE.

By H. C. Dickinson, D. R. Harper 3d, and N. S. Osborne,
Bureau of Standards.

A DETERMINATION of this constant has been made recently at the Bureau of Standards. The paper † contains a brief summary of the more important contributions on the subject, particularly of those of more recent date. The experimental work which is described at length was carried out in a water calorimeter which permitted a precision to a few parts in ten thousand in calorimetric observations.

Of two methods employed, one is the well-known method of mixtures in which an ice sample of from 100 to 200 grammes weight was allowed to melt in the calorimeter, cooling the water. The other was an electrical method of somewhat higher precision. An ice sample some 500 grammes in weight was put directly into the water and the approximate amount of energy required to melt the ice supplied electrically and measured, the small excess or deficiency being determined from the small rise or fall of temperature of the calorimeter. The usual calorimetric cooling correction was thus rendered relatively very small and the heat capacity of the calorimeter needed to be known only approximately. The ice specimens used were from commercial plate, can, and natural ice, and from ice frozen in the laboratory from double distilled water. both free from air and containing air. They were cut in the form of hollow cylinders to secure a more uniform rate of melting. The samples were kept at the uniform temperature of either— 0.72° or 3.78°-for several hours previous to the experiments, and were so weighed and handled as to introduce each into the calorimeter at the selected constant temperature with no significant error.

Altogether, the heat of fusion of each of 92 samples of pure

<sup>\*</sup> Communicated by the Bureau.

<sup>†</sup> Reprint 200, Bulletin of the Bureau of Standards.

ice was determined by one of the two methods. The results of the first half of these observations, made before the best experimental conditions were secured, indicate no differences between the heats of fusion of the different kinds of ice greater than the limits of precision,—that is, about one part in a thousand. The latter half show no difference as great as one part in five thousand between the commercial kinds of ice.

The final figure for the heat of fusion of pure ice is  $79.63 \text{ cal}_{15}$  per gramme mass.

### OBSERVATIONS ON OCEAN TEMPERATURES IN THE VICIN-ITY OF ICEBERGS AND IN OTHER PARTS OF THE OCEAN.\*

By C. W. Waidner, H. C. Dickinson and J. J. Crowe.

Through the courtesy of the Navy Department the authors were enabled to make a series of observations on board the U. S. S. *Birmingham* and the U. S. S. *Chester* between June 2 and July 10, 1912, to test the utility of accurate measurements of sea-water temperatures in detecting the proximity of icebergs.

A sensitive resistance thermometer built in the form of a plate and mounted against the inside of the ships' three eight-inch plates about six feet below the water line was connected to a Leeds & Northrup recorder. This arrangement gave a continuous record of sea-water temperatures, which would indicate variations of 0.01° or 0.02°, and proved so satisfactory that none of the several other thermometric devices carried on the trip was made use of, with the exception of deep-sea thermometers used for measuring temperatures at considerable depths.

Practically continuous temperature records were obtained for a period of about thirty days, including a score of instances where the ship was within a few hundred yards of icebergs, together with the records on approaching and leaving these bergs. In the majority of these instances the temperature fell slightly upon approaching and rose slightly upon leaving the berg, but this was by no means always true. The variations near icebergs were in general not distinguishable from those observed in other parts of the ocean. It is therefore concluded that at least in the part of

<sup>\*</sup> Reprint 210, Bulletin of the Bureau of Standards.

the North Atlantic where these observations were made, viz., near the northern route of the New York-to-Liverpool steamers, not even the most accurate measurements of sea-water temperature can be relied upon to give warning of the presence of dangerous icebergs.

Other methods of detecting the presence of ice were also tried, such as the density or salinity of the surface water, echoes, both

submarine and at night powerful searchlights.

The density of the water does not seem to depend especially upon the presence of icebergs, and neither aërial echoes nor searchlights could be depended upon to give warning of the proximity of icebergs under varying weather conditions. A few experiments upon submarine echoes gave some slight promise of reliable warnings at distances of a mile or two, but the experiments could not be pursued further because of the lack of apparatus.

The conclusions as to the value of temperature records are not in agreement with those of Prof. H. T. Barnes, of Toronto, whose observations made in regions further north indicate a rather definite small rise of temperature of the sea on approaching

icebergs.

The use of recording thermometers on shipboard, while perhaps not of great value in locating icebergs, may prove valuable in locating ocean currents and in indicating by a fall of temperature the approach to land or to shallow water.

Electric Railway in Navarre, Spain. Anon. (Elektrotechn. Zeitschr., xxxiv, 27.)—This line runs from Pamplona to Sanguesa, in the Pyrenees district in the north of Spain; the total length is 56 kilometres. It has gradients up to 5 per cent., and is intended for carrying lumber and other kinds of merchandise. It is worked on the single-phase system at 6600 volts and 25 cycles, the pressure being converted by transformers, carried on the trains, to 600 volts. The cars in some cases have four, and in other cases two, motors of 60 horsepower of the Latour type; compressed-air brakes are used to supplement the hand brakes. Portions of the line are worked with an overhead pressure of 600 volts, and special precautions are adopted to prevent the possibility of any accident to the machinery at the points of transition. This is the first single-phase line constructed in Spain, and it has been working successfully for two years.

Influence of the Cooling Medium on the Temperature-rise of Stationary Induction Apparatus. J. J. Frank and W. O. Dwyer. (Amer. Inst. Elect. Engin. Proc., xxxii, 337.)—For some time it has been admitted that the corrections to be applied to the temperature-rise of stationary induction apparatus, when operating under conditions differing from standard, require some little revision. In the first part of the paper the theoretical considerations governing the dissipation of heat from this class of apparatus are given briefly; and the influence of temperature, barometric pressure, and humidity on the emissive constants is briefly discussed. The presence of moisture was expected to have considerable influence on the temperature-rise, but a theoretical analysis shows for ordinary room temperatures the effect can be small, even though the atmosphere be saturated. Exception is made in the case of fogladen air.

The second part of the paper presents the results of some tests made to check these conclusions. Some tests were made under artificial and some under natural conditions. Recommendations for corrections to be applied and precautions to be taken are given. When possible, apparatus should be tested under conditions similar to those under which it is to operate. When these conditions cannot be maintained the following corrections should be applied: (1) Variations in Room Temperature.—On all classes of apparatus, except air-blast, no correction be applied. On air-blast the present recommendations of the A. I. E. E. be followed. On water-cooled apparatus the reference should be the ingoing water, and the temperature of this and of the room should be as near 25° C. as possible. (2) Variations in Barometric Pressure.—For self-cooled apparatus the present A. I. E. E. recommendations be followed. For water-cooled apparatus no corrections be applied. For air-blast apparatus double the present A. I. E. E. recommendations be followed. (3) Variations in Humidity.—No corrections be applied for variations in humidity except in case of fog-laden air.

Fireproof Porcelain. Heinecke. (Chem. Zeit., xxxvii, 768.)—The so-called "fireproof" porcelain cooking vessels upon the market can only be regarded as fire-resistant, since in technology the term "fireproof" is restricted to products melting above Seger cone 26. The basis of European hard porcelain is a mixture of 50 parts of clay, 25 of felspar, and 25 of quartz. A body prepared from a mixture of 30 parts Zettlitz kaolin, 52 of felspar, and 45 of alumina, burned at Seger cone 18, or preferably fused in an electric furnace, does not melt below Seger cone 35 or 36, but, since it softens without melting at high temperatures, it is advisable to replace the felspar by an intimate mixture of 1 mol. of felspar with 3 to 6 mols. of alumina. Very compact and fire-resistant masses, melting at Seger cone 37, may be prepared from a well-burned mixture of alumina and magnesia.

## THE FRANKLIN INSTITUTE

#### COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, September 3, 1913.)

> HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, September 3, 1913.

Mr. J. A. P. Crisfield in the Chair.

Amendments to the 1909 Regulations as proposed by a special sub-committee were considered and adopted in their final form.

The following reports were presented for first reading:

No. 2522.—Gaede's Molecular Air-Pump.

No. 2527.-Norton Alundum.

The following new subjects were recommended for examination:

No. 2584.—The Humphrey Pump.

No. 2585.—Ridgway's Steam Hydraulic Elevator.

The following application for investigation was accepted:

No. 2586.—Dobbin's Daylight Rods.

R. B. OWENS, Secretary.

#### MEMBERSHIP NOTES.

#### Elections to Membership.

(Stated Meeting of the Board of Managers, August 13, 1913.)

#### RESIDENT.

MR. CHAS. W. MESSNER, 3704 North Broad Street, Philadelphia, Pa.

MR. OTTO MOESSNER, Machen & Mayer Electrical Manufacturing Company, Twenty-first Street and Fairmount Avenue, Philadelphia, Pa.

Dr. Joseph P. Remington, Dean. Philadelphia College of Pharmacy, 145 North Tenth Street, Philadelphia, Pa.

MR. UTLEY WEDGE, Ardmore, Pa.

#### NON-RESIDENT.

PROF. ERNEST A. HERSAM, University of California, Berkeley, Cal. Mr. Martin Hill Ittner, Colgate & Co., Jersey City, N. J.

(Stated Meeting of the Board of Managers, September 10, 1913.)

#### RESIDENT.

- MR. CHAS. HAY SPAYD, C. E. Johnson & Co., 509 South Tenth Street, Philadelphia, Pa.
- Mr. SIMEON TRENNER, 6328 Jefferson Street, Germantown, Philadelphia, Pa.
- MR. D. ROBERT YARNELL, 316 Preston Street, Philadelphia, Pa.

#### NON-RESIDENT.

- Mr. Cecil F. Backus, Atlas Powder Company, Wilmington, Del.
- MR. A. W. K. BILLINGS, Apartado 491, Barcelona, Spain.
- Mr. George B. Chorpening, Box 197, Clarksburg, W. Va.
- Mr. H. B. SARGENT, Sargent & Co., New Haven, Conn.
- Mr. Elmer A. Sperry, The Sperry Gyroscope Company, Manhattan Bridge Plaza and Flatbush Avenue, New York, N. Y.

#### Changes of Address.

- Prof. F. W. Bushong, Mellon Institute of Industrial Research, Pittsburgh, Pa.
- Mr. Burdette Dale, 1127 Douglas Avenue, Ames, Iowa.
- Mr. Leon B. Eichengreen, Counties Gas and Electric Company, Ardmore, Pa.
- Dr. Ernst Fahrig, 207 Metropolitan Avenue, Atlantic City, N. J.
- LIEUT. R. E. GILLMOR, 57 Victoria Street, London, England.
- Mr. Fred. T. Haschka, 129 West Sixty-ninth Street, New York City, N. Y.
- Mr. EDWARD V. McCaffrey, McCaffrey File Company, Philadelphia, Pa.
- MR. F. R. PLEASONTON, International Motor Company, Plainfield, N. J.
- Dr. ISHAM RANDOLPH, 1807 Commercial National Bank Building, Adams and Clark Streets, Chicago, Ill.
- Mr. L. D. RICKETTS, Warren, Ariz.
- Dr. L. M. Tolman, 1408 Emerson Street, Washington, D. C.
- Mr. ORVILLE WRIGHT, 1127 West Third Street, Dayton, Ohio.

#### LIBRARY NOTES.

#### Gifts.

- American Society of Mechanical Engineers Transactions, vol. 34, 1912. New York, 1913. (From the Society.)
- Baldwin Locomotive Works, Record of Recent Construction, Nos. 1-40, 55 and 56. Philadelphia. (From the Works.)
- British Columbia Minister of Mines, Annual Report, 1912. Victoria, 1913. (From the Minister.)
- Buffalo, Rochester & Pittsburgh Railway Company, 28th Annual Report, 1913. New York, 1913. (From the Company.)
- Canada Department of Mines: The Nickel Industry, by A. P. Coleman, and Sections of the Sydney Coal Fields, Cape Breton, by Joseph G. S. Hudson. Ottawa, 1913. (From the Department.)

- Canadian Pacific Railway Company, Annual Report, June 30, 1913. Montreal, 1913. (From the Company.)
- Chicago Department of Public Works, 37th Report, 1912. Chicago, 1913. (From the Department.)
- D'Este Steam Engineers' Manual, 2nd edition, 1913. Boston, 1913. (From Julian D'Este Company.)
- Finland Patent Office: Yrkesinspektörerans i Finland Arsberättelser, 1911. Suomen Ammattientarkastajain Toimintakertomukset, 1911. Teollisnustilastoa 28, 1911. Industristatistik 28, 1911. Helsingfors, 1913. (From the Patent Office.)
- Illinois Railroad and Warehouse Commission, 42nd Annual Report, 1912, vols. 1 and 2.
- Institution of Civil Engineers, Minutes of Proceedings, vol. 192, 1912-13. London, 1913. (From the Institution.)
- Instituto y Observatorio de Marina de San Fernando, Anales seccion 2ª, 1912. San Fernando, 1913 (From the Institute.)
- Iron and Steel Institute Journal, vol. 87, 1913. London, 1913. (From the Institute.)
- John Crerar Library, A List of Current Medical Periodicals, ed. 2, April, 1913. Chicago, 1913. (From the Library.)
- Los Angeles Public Library, 25th Annual Report, 1912–1913. Los Angeles, 1913. (From the Library.)
- Lynn Commissioner of Water and Water Works, Annual Report, 1912. Lynn, Mass., 1913. (From the Commissioner.)
- Maryland Institute for the Promotion of the Mechanic Arts, Announcement School of Art and Design, 1913–1914. Baltimore, 1913. (From the Institute.)
- Newark Free Public Library, 24th Annual Report, 1912. Newark, N. J., 1913. (From the Library.)
- New South Wales, Department of Mines: Mineral Resources, No. 17, Report on the Cobar Copper and Gold-Field, by E. C. Andrews. Sydney, 1913. (From the Department.)
- New York State Educational Department, Annual Report, 1913, and Proceedings of the Dedication New York State Education Building, October, 1912. Albany, 1913. (From the New York State Library.)
- New Zealand Institute, Transactions and Proceedings, vol. 45, 1913. Wellington, 1913. (From the Institute.)
- Ohio Geological Survey, Bulletin 4th series, No. 17, Conemaugh Formation in Ohio, by D. Dale Condit. Columbus, 1912. (From the Survey.)
- Ontario Agricultural Societies, 13th Annual Report, 1913. Toronto, Can., 1913. (From the Ontario Department of Agriculture.)
- Oregon Railroad Commission, Sixth Annual Report, 1912. Salem, 1913. (From the Commission.)
- Pennsylvania Academy of the Fine Arts, School Circular, 1913–1914. Philadelphia, 1913. (From the Academy.)
- Pennsylvania Chestnut Tree Blight Commission, Report July 1 to December 31, 1912. Harrisburg, 1913. (From the Commission.)

Philadelphia Maritime Exchange, 38th Annual Report, 1913. Philadelphia, 1913. (From the Exchange.)

Rainfall of the Bombay Presidency, vol. 2, 1912. Bombay, 1912. From the Meteorological Department of India.)

Sayings and Writings About the Railways by Those Who Have Managed Them and Those Who Studied Their Problems. New York, 1913. (From the Bureau of Railway Economics, Washington, D. C.)

Texas Academy of Science, Transactions, vol. 12. Austin, 1913. (From the Academy.)

United States National Museum, Annual Report, June 30, 1912. Washington, D. C., 1913. (From the Smithsonian Institution.)

U. S. War Department, Tests of Metals, 1912. Index to Tests of Metals, 1881-1912. Washington, 1913. (From the Department.)

University of Buffalo, Medical Department, Sixty-eighth Announcement, 1913-1914. Buffalo, 1913. (From the University.)

University of Idaho, Catalog 1912-1913. Moscow, 1913. (From the University.)

University of Nevada, Register 1912-1913. Reno, 1913. (From the University.

Western Australia Department of Mines, Report 1912. Perth, 1913. (From the Department.)

Wisconsin Railroad Commission, Reports vols. 1-8, July 20, 1905, to March 12, 1912. Madison, 1908-1912. (From the Commission.)

#### BOOK NOTICES.

GENERAL AND INDUSTRIAL CHEMISTRY, by E. Molinari. Vol. II, Organic. Published by P. Blakiston's Son & Co. 770 pages (24.5 × 15 cm.). Price, \$6.

This is the companion volume to the "Inorganic Chemistry" of the same author, the translation of which appeared some time ago. The immediate success of both books shows that the author's plan of treating general chemistry, along with technology, in the same volume has met with wide approval. In spite of this fact, the advantages of the combination are far from obvious to the reviewer. Perhaps the point may be that the technology keeps the interest of the student alive and acts, so to speak, as a sugar-coating for the purely scientific portion.

Although the reviewer is doubtful with respect to the wisdom of the plan, he is able to give unqualified commendation to the manner in which it has been carried out. The book is much longer than its eight hundred pages would indicate, for the pages are large and the typography very close. It offers a vast amount of information, which is surprisingly accurate and modern. The translator, Dr. Pope, has done his work very well indeed.

The prices of chemicals which are of technical importance are given, often in pounds, shillings, and pence. In view of the rapid variations to which prices are subject, the value of these data is rather open to question.

In the discussion of the theory of valence on page 15 the spelling "Cooper" instead of Couper is undoubtedly a misprint. The publishers have fallen into a little unwise economy on page 70, where Fig. 90, with its Italian words in the diagram, presents a singular appearance. It would have cost very little to have a new cut made and would have avoided a blemish.

To those who think it wise to amalgamate scientific chemistry with technology, this book can be heartily recommended. Professor Molinari's "Inorganic Chemistry" on the same plan has achieved a substantial success, and the present volume is superior to its predecessor.

ROBERT H. BRADBURY.

Pennsylvania Chestnut Tree Blight Commission. Report July 1 to December 31, 1912. 67 pages, illustrations, maps, plates, 8vo. Harrisburg, State Printer, 1913.

This report gives an interesting summary of the work done in the effort to combat and eradicate the destructive chestnut tree blight.

The introduction refers to the possibility of a serious timber famine confronting the American people, and the absolute necessity for concerted action of the friends of forestry and forest conservation to avert a threatened crisis. Attention is called to the fact that it costs fully one-third more to-day to buy hemlock and other common varieties of building lumber than the same material would have cost only five years ago.

The chestnut blight occasioned a loss of many millions of dollars to the timber owners of Pennsylvania, and since the Commission decided to discontinue its operations especial interest has been aroused, as the total extermination of our native chestnut is threatened. At least a dozen other States continue the warfare against the disease. The Bureau of Plant Industry of the U. S. Department of Agriculture is coöperating in a practical manner through a large pathological force.

The reports of the several executive officers and others indicate very clearly that much progress has been made in the study of the proper treatment of infected chestnut trees. Especial attention was devoted to the utilization feature, and in this manner the owner of blighted timber was able to secure a ready market for its disposal at fair prices. The educational work enabled owners of trees to recognize the disease, and to obtain needful information of much value without cost as to the treatment of diseased trees.

The blight has been eradicated from the western part of the State, but spot infections will most likely reappear. Unless timber owners watch carefully, and destroy such infections promptly, the blight will spread rapidly and further heavy losses will follow. In Eastern and Southern Pennsylvania a large percentage of the chestnut was badly infected before the Commission was created.

Recent information shows that the chestnut blight is prevalent in China, and, therefore, probably of foreign origin. Hence there is greater hope now that continued scientific research work such as is in progress in this country

will reveal the much-needed remedial measures to prevent the threatened total extermination of our native chestnut trees.

THE SYMPTOMS OF THE CHESTNUT TREE BLIGHT AND A BRIEF DESCRIPTION OF THE BLIGHT FUNGUS, by F. D. Heald, Pathologist. 15 pages, 16 plates, 8vo. Harrisburg, Pennsylvania Chestnut Tree Blight Commission, 1913.

Bulletin No. 5 of the Commission has just come from the press and gives a complete description of the chestnut tree blight.

The disease is a parasitic fungous growth that girdles trunks, branches, and twigs of the chestnut trees, whether large or small, and kills them.

An object lesson of special importance consists in the remarkable fact that to-day there does not exist a single live chestnut tree in Greater New York, where the species thrived in great abundance only a few years ago. In Forest Park, New York, a well-known and attractive resort, there were included amongst its wealth of trees over 17,000 chestnut trees, many being of great age and rare beauty. To-day not a single chestnut tree remains in that park, all having been destroyed by the blight.

#### PUBLICATIONS RECEIVED.

U. S. War Department: Annual reports 1912 (in four volumes). Volume I, Reports of the Secretary of War, the Chief of Staff, the Adjutant-General, the Inspector-General, the Judge Advocate-General, the Quarter-master-General, the Commissary-General, the Surgeon-General, the Paymaster-General, the Chief of Ordnance, the Chief Signal Officer, the Chief of Coast Artillery. Volume II, Reports of the Chief of Engineers (without appendices). Volume III, Reports of Eastern, Central, Western, Philippines Division, Military Academy, Military Arts. Volume IV, Reports of the Chief, Bureau of Insular Affairs, Philippine Commission, Governor of Port Rico. 4 volumes, illustrations, plates, maps, 8vo. Washington, Government Printing Office, 1913.

Pennsylvania Chestnut Tree Blight Commission: Report July I to December 31, 1912. 67 pages, illustrations, maps, 8vo. Bulletin No. 5. The Symptoms of Chestnut Tree Blight and a Brief Description of the Blight Fungus, by F. D. Heald, Pathologist. 15 pages, 16 plates, 8vo. Harrisburg, State Printer, 1913.

Michigan College of Mines: Year Book, 1912–1913. Announcement of Courses, 1913–1914. 130 pages, maps, 12mo. Houghton, College, 1913.

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation Bulletin No. 2, Bibliography of Smoke and Smoke Prevention, compiled by Ellwood H. McClelland, Technology Librarian, Carnegie Library of Pittsburgh. 164 pages, 8vo. Pittsburgh, Pa., University of Pittsburgh, 1913.

Canada Department of Mines, Mines Branch: The Nickel Industry:

with Special Reference to the Sudbury Region, Ontario, by A. P. Coleman, Ph.D. 206 pages, illustrations, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1913.

U. S. Census Bureau, Department of Commerce: Forest Products No. 2, Lumber, Lath and Shingles, 1911. Forest Products No. 8, Crossties Purchased, 1911. Forest Products No. 9, Poles Purchased, 1911. 3 pamphlets, 8vo. Washington, Government Printing Office, 1913.

U. S. Office of Public Roads, Department of Agriculture: Circular No. 100, Typical Specifications for the Fabrication and Erection of Steel Highway Bridges. 25 pages, 8vo. Washington, Government Printing

Office, 1913.

U. S. Bureau of Mines, Department of the Interior: Bulletin 53, Mining and Treatment of Feldspar and Kaolin in the Southern Appalachian Region, by A. S. Watts. 170 pages, illustrations, plates, maps, 8vo. Bulletin 59, Investigations of Detonators and Electric Detonators, by Clarence Hall and Spencer P. Howell. 73 pages, illustrations, plates, 8vo. Bulletin 56, First Series of Coal-dust Explosion Tests in the Experimental Mine, by George S. Rice, L. M. Jones, J. K. Clement, and W. L. Egy. 115 pages, illustrations, plates, 8vo. Technical Paper 15, An Electrolytic Method of Preventing Corrosion of Iron and Steel, by J. K. Clement and L. V. Walker. 15 pages, illustrations, 8vo. Technical Paper 47, Portable Electric Mine Lamps, by H. H. Clark. 13 pages, 8vo. Monthly Statement of Coalmine Fatalities in the United States, May and June, 1913, compiled by Albert H. Fay. 2 pamphlets, 8vo. Washington, Government Printing Office, 1913.

U. S. Coast and Geodetic Survey, Department of Commerce: Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory at Cheltenham, Maryland, 1911 and 1912, by Daniel L. Hazard, Computer, Division of Terrestrial Magnetism. 98 pages, plates, quarto. Washington, Government Printing Office, 1913.

Harrison Safety Boiler Works: Catalogue No. 550, Section A: Live Steam Separators; B: Live Steam Separators and Receivers; C: Oil Separators; D: Vacuum Oil Separators. 4 pamphlets, illustrations, 8vo. Phila-

delphia, Works, 1913.

An Amendment to the Constitution: Prohibiting the Sale, Manufacture, and Importation of Distilled Liquor, speech of Hon. John D. Works, of California, in the Senate of the United States, June 21, 1913. 8 pages, 8vo. Washington, Government Printing Office, 1913.

Werden die Zeichen der Wechselstromtelegraphie verlängert (mit Erwiderung von Herrn Dr. K. W. Wagner). 2 pages, illustrations, quarto. Reprinted from the Elektrotechnische Zeitschrift, Heft 21. Berlin, Julius Springer, 1913.

Canada Department of Mines, Mines Branch: Sections of the Sydney Coal Fields, Cape Breton, by Joseph G. S. Hudson. Special Edition, International Geological Congress, Twelfth Session, 1913. 6 pages, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1913.

Royal Institution of Great Britain, Weekly Evening Meeting: January 17, 1913.—Some Further Applications of the Method of Positive Rays,

Prof. Sir. J. J. Thomson. February 13, 1913.—Gyrostats and Gyrostatic Action, Prof. Andrew Gray. March 14, 1913.—Great Advance in Crystallography, A. E. H. Tutton. April 4, 1913.—The Spectroscope and Organic Chemistry, James J. Dobbie, Esq., M.A., LL.D. April 11, 1913.—The Winds in the Free Air, Charles J. P. Cave, Esq., M.A. April 18, 1913.—Applications of Polarized Light, Thomas Martin Lowry, Esq., D.Sc. 6 pamphlets, illustrations, 8vo. London, Institution, 1913.

An Active Modification of Nitrogen. R. J. STRUTT. (Roy. Soc. Proc., A88, 539).—This active modification of nitrogen is produced by the electric discharge. For preparing and storing the nitrogen to be submitted to the electric discharge two 15-litre aspirator bottles are arranged as a gas-holder in the usual way, a muslin bag containing chopped phosphorus being suspended in the gas space. The gas-holder is filled with commercial nitrogen. All traces of oxygen are removed in two to three hours, and, when the fumes arising from the phosphorus have subsided, the gas is ready for use. On its way to the discharge tube the nitrogen is dried by passing it first through a column of phosphorus pentoxide, 30 cm. by 5 cm., and then through a tube packed with copper gauze and cooled with liquid air. As the gas is withdrawn from the holder the water rises and finally drowns the phosphorus, dissolving out the oxides and leaving it ready for further use. The gas-holder should be covered with a black cloth to protect the phosphorus from the action of light. Contrary to statements by other workers, the phenomena of active nitrogen are not due to the presence of traces of oxygen. Oxygen, in fact, acts unfavorably, and 2 per cent. prevents the phenomena altogether. Hydrogen and carbon dioxide are less harmful than oxygen, but even traces of water vapor are very prejudicial. Active nitrogen combines with the vapor of mercury, cadmium, zinc, arsenic, sodium, and sulphur to form nitrides which are decomposed by water or potassium hydroxide solution with the evolution of ammonia. Carbon bisulphide yields polymeric carbon monosulphide and a blue polymeric nitrogen sulphide. Sulphur chloride gives ordinary yellow nitrogen sulphide.

The Influence of "Drawing" on Metallurgical Products. L. Guillet. (Rev. Mét., x, 769.)—Drawing raises the elastic limit, increases the brittleness, and reduces the elongation of metals. Experiments made to ascertain the difference in behavior of annealed and rolled plates of pure aluminum, and of aluminum alloys, in water, and solutions of sodium hydroxide (I per cent.), sodium chloride (I, 5, and IO per cent.), hydrochloric acid (I per cent.), and magnesium chloride (I per cent.), showed that while in general the rolled plates were attacked to a greater extent than the annealed plates, this result was not invariable.

# "VOLCANIC DUST AND OTHER FACTORS IN THE PRODUCTION OF CLIMATIC CHANGES AND THEIR POSSIBLE RELATION TO ICE AGES."

### A CORRECTION.

The Editor, Journal of The Franklin Institute:

DEAR SIR:

Allow me to ask that you kindly note the following errata in my recent article on volcanic dust:

Page	for	write
137, line 4 from top	" brothers "	cousins
138, line 10 from top	. "	£4
140, line 12 from top	4.4	44
142, equation I	" $\left(l + \frac{B}{rp}\right)$ "	$\left(1 + \frac{B}{rp}\right)$
142, middle of page	" $\left(l+A\frac{l}{r}\right)$ "	$\left(1 + A \frac{l}{r}\right)$
148, line 19 from bottom	" otherwise "	other kind
162, line 4 from bottom	"spot minima"	spot maxima
168, second equation from top	"34 × 104"	34 π 104

In regard to the viscosity of dry air, it has just been shown by Millikan ( $Ann.\ der\ Phys.,\ g,\ p.\ 759,\ 1913$ ) that at the absolute temperature T

$$M_T = \frac{150.38T^{\frac{3}{2}}}{T + 124} \times 10^{-7}$$

According to this equation, page 143 should be corrected as follows:

$$M_{-55} = 1416 \times 10^{-7}$$

# Velocity and time of fall.

Height in kilometres	Barometric pressure	Centimetres per second	Seconds per centimetre
40	1.84	1.0214	0.979
30	· 8.63	0.2414	4.143
20	40.99	0.0745	13.427
15	89.66	0.0503	19.874
II	168.00	0.0408	24.492
О	760.00	0.0259	38.603

While all the foregoing corrections are desirable, they do not affect the argument nor alter in the least any of the conclusions.

Yours truly,

W. J. Humphreys.

# CURRENT TOPICS

Uranium and Radium. C. L. PARSONS. (Min. and Eng. World, May 10, 1913.)—All the radium placed on the market in the last few years has been produced in Europe, yet a large portion of this output has come from American ores. At least 20 to 25 tons of high-grade pitchblende have been exported. last year carnotite containing 28.8 tons of pitchblende, from which 11.43 grammes of radium bromide could be obtained, were pro-All this ore was shipped abroad for the extraction of The value of the radium salts extracted would be about \$530,000. The total supply of radium salts from all other sources was 3.65 grammes of radium chloride, basing the production of the Austrian mines for 1912 upon that of 1911, which is known. Small quantities of pitchblende have been found in Connecticut, and in the feldspar quarries of North Carolina. Practically all the American output has come from the mines in Quartz Hill, Gilpin County, Colorado. Carnotite consists chiefly of potassium uranyl vanadate, but also contains small amounts of barium and calcium compounds. Necessarily it also contains radium, although it has not yet been definitely established that the uranium and radium are in equilibrium as they are in pitchblende. In carnotite the amount of radium is not far from the equilibrium ratio, and in the calculations given above an allowance of 10 per cent, has been made to cover this possible deficiency. The more important deposits are scattered over Colorado and Utah. Carnotite always carries vanadium as well as uranium and radium, but is purchased almost wholly on its radium content, comparatively little being allowed for its vanadium. Ore with 2 per cent. uranium oxide is now worth approximately \$75 per ton f. o. b. New York. In mining these carnotite ores probably 5 tons of material capable of concentration are wasted for every ton sent to market. One of the problems before the Bureau of Mines is to develop methods for concentrating these ores.

Cellulose from Pea and Bean Stalks. O. Reinke. (Chem. Zeit., xxxvii, 601.)—On digestion with not more than 6 to 7 per cent. of caustic soda, waste pea and bean stalks readily yield cellulose in larger proportion and better quality than that obtained from asparagus stalks. The cellulose is easily bleached by bleaching powder liquor, and still better by a 1 per cent. solution of potassium permanganate, followed by sulphurous acid. The celluloses are free from knots and consist of small fibres, fine, woolly, and brilliant white. The cellulose is very suitable for the manufacture of nitrocellulose, viscose, etc.

Electrical Emissivity of and Disintegration of Hot Metals. J. A. HARKER and G. W. C. KAYE. (Roy. Soc. Proc., A 88, 522.)— The metals were heated by alternating current, mostly in nitrogen at reduced pressure. Positive electricity was emitted at temperatures from about 1000° C. to 1400° C.; and for metals which melt within this range a sudden and marked increase in the positive current often occurred at the melting-point, probably owing to the sudden release of occluded gas. The positive current appears to be increased in presence of oxygen. Negative electricity predominates at higher temperatures, and increases rapidly with the temperature. With carbon in air at atmospheric pressure, a negative ionization current of 3½ ampères was obtained. At moderate pressures the negative currents appear to be largely increased when considerable sputtering of the metal occurs; they are probably due to a chemical reaction between the metal and the surrounding gas. It is considered that the deposits obtained in these experiments are due not only to volatilization and condensation, as ordinarily understood, but also to straight-line emission of particles (compare Reboul and De Bollemont). Carbon becomes soft and plastic, and readily sublimes, at about 2500° C. A metal tube cooled by water was surrounded by a carbon tube, and the latter was heated by low-voltage alternating current to about 2500° C., hydrogen being passed between the two tubes. After about 30 minutes, the metal tube was coated with a deposit of carbon sufficiently hard and coherent to be removed in short lengths. It is suggested that carbon of high purity could be obtained in this way by fractional distillation.

Colorado Coal Production. (U. S. Geological Survey.)—Coal mining as an industry in Colorado began in 1864, when a production of 500 short tons was recorded. In 1876 the production reached for the first time a total exceeding 100,000 tons, and six years later, in 1882, it had reached the million-ton mark. Since that date the increase has been almost uninterrupted. The production exceeded 3,000,000 tons in 1890; 10 years later it had grown to over 5,000,000 tons, and in 1910 it exceeded 11,000,000 tons, but in 1912 it fell just below the 11,000,000-ton mark.

Cistern Filters Do Not Remove Germs. (U. S. Geological Survey.)—Cisterns that are properly constructed and receive rain water from roofs generally afford water of good sanitary quality, but if water of doubtful quality is stored in cisterns the supply is, of course, not safe for domestic use. Filters used in connection with cisterns are of value in making the water clear, but are generally of no value in removing disease germs. Many cisterns are divided into two parts by a brick wall, the water being admitted into one compartment and drawn from the other. In such cisterns the water passes through the brick and in that way is improved in clearness and color, but not generally in sanitary quality.

Extraction of Thoria from Monazite Sand. F. WIRTH. (Chem. Zeit., xxxvii, 773.)—The formation of sparingly soluble double sulphates of earth metals is avoided by generating the anion of hypophosphoric acid directly in the acid liquor resulting from the decomposition of monazite sand. This is done by the anodic oxidation of copper phosphide in the solution, after first neutralizing the free acid present, so far as to leave the phosphates just dissolved. With an electromotive force of about 10 volts the hypophosphate ions are at once converted into the insoluble thorium salt. Oxidizers, such as hydrogen peroxide, which give ozone on electrolysis, facilitate the process. Thorium may also be precipitated by alkali hypophosphate from feebly alkaline solution (e.g., of the tartrate), and the solubility of thorium hypophosphate in a large excess of ammonium oxalate may be utilized for separating thorium, in alkaline solution, from trivalent earths, which are insoluble in ammonium oxalate. The thorium hypophosphate is treated as previously described. Cerium may be detected in neutral solution by adding 5 c.c. of 10 per cent. ammonium tartrate solution and 5 c.c. of dilute ammonia; the solution becomes yellow or yellowish-brown on boiling, or in the cold with 0.1 to 0.5 per cent. of cerium. Hydrogen peroxide gives a brown precipitate of cerium peroxide with concentrated alkaline solutions of cerium tartrate, and a coloration may be detected with 0.0002 gramme of cerium peroxide in 100 c.c.

The Periodic System and the Radio-Elements. A. S. Russell. (Chem. News, cvii, 49.)—It has been recognized that some of the longer-lived radio-elements, such as Ra, RaF, and RaEm, have definite places in the periodic system of the chemical elements. In this paper the whole of the radio-elements are dealt with. The rules given are: (1) Whenever an a-particle is expelled by a radio-element the group in the periodic system to which the resultant product belongs is either two units greater or two units less than that to which the parent body belongs. (2) Whenever a  $\beta$ -particle or no particle is expelled, with or without the accompaniment of a  $\gamma$ -ray, the group in the periodic system to which the resultant product belongs is one unit greater or one unit less than that to which the parent product belongs.

Devitrification of Quartz Glass. A. C. MICHIE. (Chem. Zeit., xxxvii, 589.)—The transformation of quartz glass into cristobalite at high temperatures was noted by Day and Shepherd, and more recently by Rieke and Endell. Thomas stated that small additions of titania or zirconia counteracted this tendency. The author contradicts this statement and affirms that vitreosil, the English fused silica, is less liable to devitrification than siloxide and other glasses which contain zirconia or titania. Seger and Cramer support this view. The method of testing consists of heating the ware at high temperatures in oxidizing and reducing atmospheres.

Coal-Dust Explosions. (4th Report of Explosions in Mines Committee.)—While there is no well-defined border line between "inflammation" and "explosive combustion" in the case of gaseous mixtures, a distinction may be drawn in the case of mixtures of coal dust and air. During the "inflammation" of dust from bituminous coals the flame is largely propagated by the burning of gases distilled from the dust, but during "explosive combustion the portion of each dust particle that aids in propagating the flame is burned as a whole. A coal dust containing 16 per cent. of volatile matter caused an explosion as violent as one caused by a dust containing 35 per cent. of volatile matter, while explosions of equal or greater violence were caused by wood charcoal. Experiments made by R. V. Wheeler in the Altofts gallery are described which confirm this conception of two distinct stages—"inflammation" and "explosive combustion "—in the combustion of mixtures of coal dust and air. The combustion of the mixture was of the nature of an "inflammation" until it had travelled some distance along the gallery, when it was suddenly converted into "explosive combustion," marked by a sudden and considerable rise of pressure. Attention is drawn to the connection between these results and the view advanced by Blackett (Trans. Fed. Inst. Min. Eng., 1894, vii, 54) as to the effect of a "pioneering cloud" in dust explosions. The experiments show that, for a propagating inflammation to take place in a mine, the concussion of a blown-out or overcharged shot, or of a firedamp explosion, is not essential. A flame, without any concussion, can ignite a ready-formed dust cloud, and the inflammation will spread through the cloud with increasing velocity and, if the conditions remain favorable, will ultimately change to "explosive combustion." Constrictions or obstructions cause the transition from inflammation to explosive combustion to take place at a much earlier period than in a smooth gallery, though they do not necessarily increase the ultimate violence of the explosion.

Refractive Index of Selenium. W. S. GRIPENBERG. (Phys. Zeitschr., xiv, 123.)—When melted selenium is pressed between plate glass, sheets from 20 to 250  $\mu$   $\mu$  in thickness may be obtained. Notwithstanding the rapid cooling, small circular portions, less than 0.2 mm. in diameter, become crystalline. They show much greater absorption of light than the amorphous selenium, and have a higher refractive index. The interference colors are of a higher order in the crystalline selenium than in amorphous selenium. They show that the refractive index is from 1.16 to 1.27 times greater. This gives a refractive index 3.5 for sodium light, or the highest refractive index known among elementary substances. This result was confirmed by making a film of selenium on glass by cathode disintegration and crystallizing one-half of it. The crystallized half showed narrower interference rings than the amorphous half, the diameters being as 4 to 5.

Influence of Phosphorus on the Properties of Iron. E. D'AMICO. (Ferrum, x, 289.)—Three series of experiments were made on the natural, annealed, and chilled material of 12 samples with increasing phosphorus content, 0.012 to 1.242 per cent. chemical composition, specific gravity, and metallographical characters are given. The conclusions reached are: The increase in hardness is nearly proportional to the phosphorus content, about 12 Brinell units per o.1 per cent. increase. Elasticity is increased about 2.7 kilos per square millimetre per 0.1 per cent. Tensile strength increases until 0.5 per cent, phosphorus is reached, beyond which it decreases. Expansion and contraction decrease as the tensile strength increases with low phosphorus contents; but with high phosphorus they are practically nil. Above 0.24 per cent. phosphorus the metal is very brittle. The electric conductivity is lowered, but the magnetic properties are influenced only by a high phosphorus content, the latter counteracting the effect of the preliminary treatment of the material. Numerous tables, diagrams, and microphotographs are given.

Rare Metals in Copper. Anon. (Brass World, ix, No. 8, 279.)—Some copper ores contain considerable quantities of rare metals, and many copper refiners take the precaution of saving them by the electrolytic refining process. In a paper in the Transactions of the American Institute of Mining Engineers, A. Eilers gives the proportions of rare metals obtained from several varieties of copper. The copper from Garfield, Utah, contains in 5000 tons:

Gold	14,400 ounces
Silver	174,000 ounces
Platinum	17 ounces
Palladium	59 ounces
Selenium	2,800 pounds
Tellurium	277 pounds
Bismuth	305 pounds
Nickel	2,000 pounds

Selenium was present in all the varieties of copper examined, and nearly always in greater quantity than the tellurium. Some of the copper contained no tellurium.

Whale Oil Refining. Anon. (Board of Trade Jr., May 29, 1913.)—A Norwegian-German company near Fredrikstad, with a capital of \$833,500, has been formed to work a new German method of oil refining. The Hafslund Falls will generate the electric power required, and will also manufacture by electrolysis the hydrogen required to convert the purified whale oil into a solid neutral fat. It is estimated that the factory will consume about 300 barrels of oil daily.

Concentration of Pitchblende. H. E. Wood. (Eng. and Min. J., xcv, 1164.)—Numerous commercial tests have shown that the usual process of concentrating pitchblende ores to remove silica results in a loss of upwards of 50 per cent. of the pitchblende. In the following process about 90 per cent. of the pitchblende is recovered, and the concentrate will contain from 45 to 56 per cent. uranium oxide. The ore is crushed to 20-mesh size, roasted, the iron oxide separated magnetically, and then the uranium oxide by a wet or dry gravitation process. In the case of carnotite ores the vanadium oxide may be removed by shaking the crushed ore with water and collecting the slime for further concentration. By this means an ore containing from 1 to 2 per cent. of uranium and vanadium oxides will yield a concentrate containing from 75 to 85 per cent. of the oxides. After removing the vanadium and uranium the ore can be used in the preparation of radium.

Pulverized Coal as a Fuel. H. R. BARNHURST. (Met. and Chem. Eng., xi, 127.)—It is stated that coal properly pulverized and burned may be made to yield higher economic results than are attainable by any other means. The proper conditions are: (1) The coal must be dried to not exceeding 1 per cent. of moisture. (2) It must be pulverized to a high degree of fineness. (3) It must be projected into a chamber hot enough to cause instant deflagration. (4) It must be supplied with air sufficient to yield the oxygen necessary to burn the carbon at once to CO<sub>2</sub>. These four requirements are discussed in detail, with special attention to (3) and (4), which have hitherto not been sufficiently considered by engineers. Very high temperatures are attainable with pulverized fuel; thus

```
I pound carbon with 11.6 pounds air
I pound carbon with 13.92 pounds air
I pound carbon with 16.24 pounds air
I pound carbon with 18.56 pounds air
I pound carbon with 20.88 pounds air
I pound carbon with 23.20 pounds air
I pound carbon with 23.20 pounds air
I pound carbon with 23.20 pounds air
I pound carbon with 11.6 pounds air
I pound carbon with 13.92 pounds air
I pound carbon with 13.92 pounds air
I pound carbon with 23.20 pounds air
I pound carbon with 13.92 pounds air
I pound carbon with 23.90 pounds air
I pound carbon with 16.24 pounds air
I pound carbon with 25.60 pounds air
```

In practice the fireman soon learns how to judge whether the fire is hot enough by its color and the length of the flame. The better the conditions, the shorter and whiter the flame will be. The temperature is generally kept down to the limit desired by admitting excess air. With regard to protecting the furnace lining against the destructive effect of these high temperatures, much of the trouble has arisen from the gases impinging on the surface walls at points where the direction of the gas travel changes, and from too high velocity of the gases due to contracted ports. If the greater part of the heat is largely absorbed by the charge, the waste gases will be proportionately less active in scouring the brickwork. In almost any construction, except perhaps a rotary kiln, it is necessary to change the

direction of the gases on their passage to the flue. This change of direction causes the gases to impinge upon the diverting bricks with an energy proportional to their velocity. At these points the brick can be protected by a system of water-cooled pipes embedded in the walls. The brick may frit to some extent until the protected area is reached, when the fritting will be arrested. The surprisingly small quantity of water which it is necessary to introduce to keep the temperature of the outlet below 200° F. proves that the cooling effect is limited to a prevention of cumulative action, and is no perceptible drawback to the efficiency.

Manufacture of Chilled Iron Car-wheels. F. C. Weber. (Metal. and Chem. Eng., xi, 92.)-It is difficult to make plain, chilled iron car-wheels of uniform quality from the usual mixture of pigiron, old car-wheels, and steel and malleable iron scrap. Uneven composition is often shown by brown spot flaws between the tread and the flange; and these brown spots may be due to the viscosity of the molten iron at the time of pouring, which prevents it filling the mould solidly. This becomes oxidized to Fe<sub>3</sub>O<sub>4</sub>, and during service becomes a well-defined crack, which is gradually covered with Fe<sub>2</sub>O<sub>3</sub>. Chilled iron car-wheels are also subject to defects technically known as "bones." These are of two distinct kinds: they may be a segregation of slags or may consist of a hard spot of steel. The latter case may arise from the steel scrap fed into the cupola with the mixture not being thoroughly melted. The segregation bones of slag get into the wheel when slag flows through the spout of the pouring ladle and by the segregation of slags within the body of the metal. These slag bones can be avoided by exercising care in keeping slag from flowing into the pouring ladles and by scavenging or cleansing the molten iron. An alloy for cleansing the iron is recommended, which contains 1/4 per cent. iron, 12 titanium, 8 boron, and 6 per cent. aluminum, silicon, etc. The titanium of this alloy combines with the occluded nitrogen, the boron fluxes out the slags, and the aluminum reduces any oxides present. In use the alloy is placed on the bottom of the pouring ladle and the molten iron run in. There is also a description of a new machine for testing car-wheels.

"Duriron": a Non-corrosive Iron Alloy. J. R. PITMAN. (Eng. News, lxix, 563.)—A practically non-corrosive iron alloy has recently been placed on the market under the name "Duriron." Apparently the only material which attacks it appreciably is concentrated phosphoric acid. Its composition is not given, but it is said to be 10 per cent. lighter than cast iron, which it resembles; to contain at least 10 per cent. silicon, and to have a tensile strength of 15,000 pounds and a compression strength of 70,000 pounds per square inch. Its use is chiefly in acid pipe-line fittings, valves, and in chemical and celluloid works. It is only available in the form of castings, and can only be machined by grinding.

Heat Treatment of Gun Metal. Anon. (Amer. Mach., xxxviii, No. 24, 980.)—A paper presented to the British Institute of Metals on this subject states that the conclusions drawn from tests made on a metal containing 88 per cent. copper, 10 per cent. tin, and 2 per cent. zinc were as follows: No improvement may be expected from quenching, which lowers the strength of the material. Simple annealing of the metal for 30 minutes increases very considerably its strength and elongation; the maximum results being obtained after annealing at 700° C. The homogeneity and other physical properties of the metal are correspondingly improved, but particularly the capability of the castings to withstand hydraulic pressure. These results are considered to be due to the removal of the eutectic from the microstructure, which after annealing shows only the crystals of a solid solution. It is thought that this heat treatment will minimize the corrosion of the metal.

Conduction of Heat and Thermal Resistivity. C. P. RAN-DOLPH. (Amer. Electrochem. Soc. Trans., xxi, 545.)—Investigations of the resistance to the flow of heat exhibited by various substances. These experiments were made with a view to various practical devices depending on heating by electricity. Thermal resistance is defined as the difference in temperature in degrees Centigrade per watt of heat-flow. The general conclusions are: (1) There are no materials which can be called thermal insulators in the same sense as is meant in the case of electrical insulators. (2) There is no method of preventing the flow of heat as good as an evacuated space. (3) The organic fibrous materials such as eiderdown, wool, etc., are the best insulators found. (4) Materials relatively coarse, such as poplox, may be very good insulators at low temperatures (100° C.), but have a very great negative temperature coefficient. (5) Increasing the density of a material by compression increases its resistivity. This only holds true up to a certain limit. (6) The thermal conductivity of bricks varies inversely as the temperature of burning. Details of the thermal resistivity of various organic materials, insulators containing asbestos, miscellaneous materials such as mineral wool, and ceramics, are given in a series of tables.

Metallic Beryllium (Glucinum). F. FICHTER and K. JABLCZYNSKI. (Ber., xlvi, 1604.)—The metal was obtained by the electrolysis of a fused mixture of the beryllium and sodium fluorides (2 mols.: 1 mol.). The product was purified from adherent oxides by centrifuging the fine powder in a mixture of ethylene bromide and alcohol of specific gravity 1.95. It was then compressed into cylinders and fused. After fusion the metal has a specific gravity of 1.842, melts at 1280° C., and does not volatilize at 1900° C. Its electric conductivity at 20° C. is 5.41 × 104 reciprocal microhms per cubic centimetre, and its hardness is 6–7 on Mohs's scale. Its apparent inertness toward water is due to a film of oxide.

Cementing of Belts. Anon. (Amer. Mach., xxxviii, No. 24, 980.)—From the Railway and Locomotive Engineering.—The following mixture is said to give satisfactory results: Take a good glue, add an equal weight of American isinglass, place in a glue-pot and add enough water to cover. Let the mixture soak for 10 hours, then bring it to boiling and add pure tannin until the mass appears like the white of an egg. Apply warm. Buff the grain of the leather where it is to be cemented, rub the joint surfaces solidly together, and let it dry for a few hours, when the belt will be ready for use. Tannin or tannic acid is an astringent substance used in converting hides into leather, and produces a surface on a cemented belt similar to the original leather.

Simple Method of Determining the Densities of Powdered Minerals. M. Billy. (Comptes Rendus, clvi, 1065.)—In measuring the density of a powdered metal, etc., error is introduced owing to the presence of innumerable small gaseous envelopes surrounding the solid particles. To avoid this, the author replaces the air held by the powder by carbon dioxide and weighs the substance, not in water, but in an approximately normal potassium hydroxide solution, which has been previously boiled. The density of the alkaline solution alone is determined in the same way, the pycnometer being filled with carbon dioxide before the alkali is introduced. A special apparatus has been designed to facilitate these operations. The method was tested by the examination of powdered glass, the density of which had been measured prior to powdering. Whereas other methods give results accurate to about 1 part in 300, this method showed an accuracy of the same order as that of the balance employed, viz., 1 in 3000. It would, therefore, seem advisable to powder all solids before measuring their density so that the absence of enclosed bubbles or fissures may be insured.

Comparison of Zinc Chloride with Coal-tar Creosote for Preserving Cross-ties. H. F. Weiss. (Elect. Rwy. Journ., xli, 151.)— A great many preservatives have been tested for cross-ties, but zinc chloride and coal-tar creosote are far more extensively used than any others. These two are compared as preservatives for cross-ties, and the data do not apply to poles, piling, or other products. The most noteworthy points are: (1) Zinc chloride and coal-tar creosote, when used under normal conditions, are both effective preservatives of cross-ties, and there is little to choose between them as to the annual charges. (2) Creosoted ties generally cost initially more than Burnettized ties, the cost of treatment being two to three times as much. (3) Creosoted ties last, on an average, longer in the track than Burnettized ties, hence require less frequent renewals and changes in the road-bed. (4) If creosote advances appreciably in price the probable result will be that more ties will be treated with zinc chloride.

Fixation of Nitrogen by Alumina and Carbon. Tucker and READ. (Amer. Electrochem. Soc. Trans., xxii, 57.)—The object of the investigation was to discover whether nitrogen would combine with a heated mixture of alumina and carbon, or with the products arising from the heating of such a mixture, and to study the best conditions for effecting the reaction. The first experiments were made in a wire-wound electric resistance furnace. In order to obtain higher temperatures a granulated carbon furnace was used, through which a tube passed for holding the charge, heated by a single-phase alternating current. At first several porcelain tubes were used, embedded in the granular carbon resistor. These porcelain tubes were unable to stand the sudden changes in temperature. This was overcome by the use of a graphite tube, with a bore 5% inch in diameter. This tube had accurately-fitted stoppers of graphite, through which the nitrogen was passed by means of metallic tubes threaded into the stoppers. The charge was contained in a graphite boat. From the result of the few experiments given it is clear that, under proper conditions, there should be no difficulty in producing aluminum nitride containing 30 per cent., or even more, nitrogen. This should be preferable to calcium cyanamide, which averages 17 to 20 per cent. fixed nitrogen.

Atmospheric Electrification during Dust Storms. V. H. Jackson. (Nature, xci, 213.)—At Patna, in North India, the westerly winds, which occur in the daytime from the middle of March till June and raise a great deal of dust, are associated with a large negative potential gradient. On one occasion a negative gradient of about 1650 volts/m was measured. It is concluded that probably from 9 A.M. to 6 P.M. on the majority of days from March to June the potential gradient over a large portion of Northern India is negative and very large. This association of negative potential gradient with dust storms is similar to that found by Rudge in South Africa.

Law of Volatility in Chemical Reactions. C. Matignon. (Comptes Rendus, clvi, 1536.)—Matignon generalizes Berthollet's "law of volatility" in the following form: "Every system of liquid or solid bodies, which is capable of giving rise to a system containing volatile substances, will undergo reaction in that sense at a convenient temperature." The reaction 2 Al + 3 MgO = 3 Mg + Al<sub>2</sub>O<sub>3</sub> is possible because magnesium is quite volatile at comparatively low temperatures. In the same way it is probable that barium oxide will be reduced by silicon, owing to the relative volatility of the barium produced. The law can also be extended thus: A reaction which has volatile bodies in its initial stage and also in its final stage is facilitated when the number of volatile molecules in the final stage is greater than that in the initial one,—i.e., of two reactions which are equally endothermic, the one complying with this condition will take place at a lower temperature.

The Protein Substances of Yeast. P. THOMAS. (Comptes Rendus, clvi, 2024.)—Starting with partially-autolyzed yeast two different proteins were isolated. The first contains nitrogen 16.10 to 16.18 per cent., phosphorus 1.75 to 1.83 per cent., and sulphur 0.38 per cent., and its properties are intermediate between casein and vitellin, but more closely resemble the former. The second, which is designated *cerevisin*, appears to be a typical albumin. It contains nitrogen 16.3 to 16.4 per cent., sulphur 0.89 to 0.94 per cent., and phosphorus up to 0.7 per cent.; this phosphorus is probably present as an impurity owing to imperfect purification. Cerevisin is soluble in water and is not precipitated by acetic acid or magnesium sulphate, or by adding an equal volume of a saturated solution of ammonium sulphate to its solution. On heating the neutral or slightly acid solution it becomes turbid at about 40° C. and gives a slight coagulum at 41° C. The filtered solution remains clear up to 49° C., and yields a second coagulum at 50° C. On further heating abundant precipitation occurs between 55° and 58° C., and coagulation proceeds continuously up to 70° C. Cerevisin gives the usual precipitation and color reactions; the glyoxylic reaction (tryptophan) is particularly distinct.

The Equipment of the New Terminal Post Office in New York. L. B. MARKS and J. E. WOODWELL. (Electr. World, Ixi, 39.)—Herein is described the electrical and mechanical equipment. wiring and illumination of the Government building over the Pennsylvania Railroad yards. The total volume of business in the building will eventually represent an average of over 5,000,000 pieces of mail matter daily, which is about double the present amount. Two classes of machinery are provided—one for handling the outgoing and one for the incoming mail. There are eight overhead belt conveyors for the outgoing mail, driven by motors of the semi-enclosed type, designed for 650 volts. There are two sources of energy for operating the mail handling motors, one consisting of separate feeders from the main switchboard in the power plant, and the other of a connection taken from the third rail operating the train service. The electrical equipment of the post office consists of a complete system of conduits and wiring for lighting and motor service, with feeders and meter switchboard and separate distributing switchboards. Details are supplied.

Alum Mountain in New Mexico. Anon. (Chem. Trade 1., June 21, 1913.)—The alum mountain near the Gila River, in southwestern New Mexico, is 900 feet high, and covers two square miles, and the United States Geological Survey finds it to be so pure that for many uses it can be marketed in the natural state. As a probable future source of aluminum this material has a still greater value. Enormous beds of lignite near-by offer power at one-fourth to one-half the cost of hydro-electric power.

Separation of Graphite from Iron-Silicon Alloys. G. CHARPY and A. CORNU. (Comptes Rendus, clvi, 1616.)—Silicon in steels, as in pig iron, facilitates the separation of the carbon as graphite when the alloy is heated to a suitable temperature. The phenomenon is, however, complicated in steels by the fact that the total carbon may be lower than the maximum quantity that the steel is capable of dissolving at a high temperature. The separation of graphite in this way from a steel is therefore observable through a range of temperature rising from T°, the temperature at which separation begins, and which is lower as the percentage of silicon is higher, to T'°, at which the solubility of graphite in steel corresponds to the total carbon present, and which is higher as the percentage, not only of carbon but also of silicon, is higher. In steels low both in carbon and silicon T' may be below T, and then no separation of graphite occurs.

Aërodynamics. A. Lechner. (*Phys. Zeitschr.*, xiv, 210.)—Determines both theoretically and experimentally the "phygoid" or trajectory of a flying model for the case when it moves in a liquid. The phygoid theory is directly applicable to liquids if the laws of resistance are the same as in air. The paths can either be circles or waves, according to the initial velocity and direction, and in the case of instability "tumbling" curves will be obtained. This was verified by means of flying models of thin sheet metal cut out in the rough outline of birds and tipped with lead. These were released in or projected into water.

Pressure in the Solar Atmosphere. C. E. St. John. (Science, xxxvii, 28.)—An investigation involving the comparison of arc and solar spectra of iron is being undertaken at the Mount Wilson Solar Observatory with the 150-foot Tower telescope. The preliminary results show that the solar lines of iron, classified in accordance with their displacement in the solar spectrum, fall into the classes suggested by Gale and Adams in their study of pressure-shift under laboratory conditions, and indicate pressures in the solar atmosphere varying from 0.7 to 6.5 terrestrial atmospheres for the different groups.

Preparation of Molybdenum and Tungsten Carbides. S. Hilpert and M. Ornstein. (Ber., xlvi, 1669.)—The carbides of molybdenum and tungsten can be obtained by heating the finely-powdered metals, or their tri-oxides, in a current of carbon monoxides or of a mixture of methane and hydrogen (I:I by volume). By the action of carbon monoxide on molybdenum at 600° and 1000° C., Mo<sub>2</sub>C is obtained; at 800° C. products ranging from MoC to  $Mo_2C_3$  are obtained. Tungsten yields  $W_3C_4$  by the action of carbon monoxide at 1000° C., and WC by the action of methane and hydrogen at 800° C.

Hertzian Oscillations from Cathode. K. BIRKELAND. (Comptes Rend., clvi, 879.)—Electrical oscillations are found to be produced by the intermittent discharge emanating from isolated spots on the cathode of a Crookes tube.

Lag in the Combustion of Gaseous Mixtures. TAFFANEL and LE FLOCH. (Comptes Rend., clvi, 1544.)—The occurrence of lag in the inflammation of methane-air mixtures is not due to the presence or absence of moisture. The probable cause is the relatively slow rate at which the velocity of reaction increases with the temperature compared with the rate in other inflammable mixtures which do not exhibit the lag.

Tri-Ferrous Carbide (Cementite). O. RUPP and E. GERSTEN. (Ber., xlv, 63.)—Pure cementite was prepared by heating a yiron, containing 4 per cent. of carbon and very free from impurities, to whiteness for an hour with powdered carbon. Analysis showed it to contain 93.28 per cent. of iron and 6.69 per cent. of carbon (theory 93.33 and 6.67). It was a dark-gray or bronzecolored substance, consisting of sphœrolithic aggregates of needlelike crystals, extremely brittle, and with a hardness slightly above that of calcite (whence it follows that the hardness of chilled irons is not due to cementite as such, but to its solid solution in  $\gamma$ -iron). Its specific gravity was 7.396, and specific volume 24.34, while that calculated from the specific volumes of its constituents is 27.84, showing that contraction occurs during its formation. To determine its heat of formation it was burnt in oxygen in a bomb calorimeter,  $Fe_3C + 3O_2 = Fe_3O_4 + CO_2$ , the product analyzed and allowance made for the amount of iron burnt only to ferrous oxide; the result per gram-molecule was 375.1 calories. The heat of combustion of iron to ferroso-ferric oxide was similarly determined for two specimens, with results agreeing closely among themselves and in good accord with Berthelot's figure obtained by a totally different method: per gram-molecule 265.2 calories. Adding to this the heat evolved in the combustion of an atom of graphite carbon to carbon dioxide, 94.8 calories, we get 360 calories as the sum of the heat of combustion of the separate constituents of cementite. Hence cementite is endothermic, and the reaction  $Fe_3 + C = Fe_3C$  absorbs 15.1 calories. This is entirely at variance with Campbell's result, which was confirmed by the calculations of Schenk, Semiller, and Falcke, but confirms a deduction of Ruff's from a study of the equilibrium diagram of the ironcarbon alloys.



# **JOURNAL**

OF

# THE FRANKLIN INSTITUTE

DEVOTED TO SCIENCE AND THE MECHANIC ARTS

Vol. CLXXVI

NOVEMBER, 1913

No. 5

# EVIDENCE BEARING ON THE SOLVATE THEORY OF SOLUTION.\*

BY

#### HARRY C. JONES.

[ The investigations referred to in this paper have been largely carried out with the aid of grants from the Carnegie Institution of Washington.

This paper has been written in response to a request from the Editor of the JOURNAL OF THE FRANKLIN INSTITUTE, to summarize for this journal the experimental evidence obtained in my laboratory, bearing upon the solvate theory of solution as it originated here about fourteen years ago.]

The solvate theory of solution was proposed from this laboratory in 1900 <sup>1</sup> to account for certain apparently abnormal freezing-point lowerings produced by certain electrolytes when dissolved in water. These had been observed by Jones and Ota, <sup>2</sup> and Jones and Knight, <sup>3</sup> and a large number of such cases were brought to light by Jones and Chambers, <sup>4</sup> and by Chambers and Frazer, <sup>5</sup> working with Jones.

Jones and Getman <sup>6</sup> then took up this problem systematically, and found that this abnormally great lowering of the freezing-point of water produced by dissolved substances in concentrated

Copyright, 1913, by THE FRANKLIN INSTITUTE.

<sup>\*</sup> Communicated by the author.

<sup>&</sup>lt;sup>1</sup> Amer. Chem. Journ., 23, 89 (1900).

<sup>&</sup>lt;sup>2</sup> Ibid., 22, 5 (1899).

<sup>&</sup>lt;sup>3</sup> Ibid., 22, 110 (1899).

<sup>4</sup> Ibid., 23, 89 (1900).

<sup>&</sup>lt;sup>5</sup> Ibid., 23, 512 (1900).

<sup>&</sup>lt;sup>6</sup> Zeit. phys. Chem., 46, 244 (1903). Phys. Rev., 14, 146 (1904).

<sup>[</sup>Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.]

solution was a more or less general phenomenon. It was manifested to the greatest extent by those substances which crystallize from aqueous solutions with the largest amounts of water of crystallization. Indeed, the magnitude of the freezing-point lowering was nearly a linear function of the water of crystallization.

This suggested that there is probably some connection between the two sets of phenomena. The question was, what is this connection? Water of crystallization is essentially water of hydration out of solution. A salt brings with it out of solution a certain amount of water, which it can hold in more or less stable equilibrium under the conditions under which it ordinarily exists. Other things being equal, that salt which can hold the largest amount of water in combination as water of crystallization out of solution, would be the salt which, in solution, would combine with the largest amount of water. Indeed, it is difficult, on a priori grounds, to see why a salt should combine with water when leaving the solution, and hold this water with the stability with which water of crystallization is held; and not combine with water when in solution,—i.e., when in the presence of a large amount of water.

These were the facts at that time available, and this the line of thought which led me, in 1900, to suggest, as a tentative explanation of the apparently abnormally large freezing-point lowerings produced especially by concentrated solutions of most substances, what was then called the hydrate theory of solution. The idea was that when substances are dissolved in water they combine with more or less of it; the amount depending upon the nature of the dissolved substance. If this suggestion were true, if dissolved substances do combine with a part of the water present, thus removing it from the field of action so far as solvent is concerned, then we could account satisfactorily for the large freezingpoint lowerings. There being less solvent present than we supposed, the lowering of its freezing-point by the dissolved substance would be greater than we would expect; since freezing-point lowering is proportional to the ratio between the number of parts of the dissolved substance and number of parts of the solvent.

Further, this explanation would also account for the fact that the freezing-point lowerings become more and more abnormally great as the solution becomes more and more concentrated. The more concentrated the solution the larger the total amount of water held in combination by the dissolved substance. Hence, the smaller amount of water remaining free and, therefore, playing the role of solvent. Consequently, its freezing-point would be lowered more and more.

This explanation would, then, account for all of the facts observed; the question is, Is it true? There might be other explanations that would account for these facts as well as, or better than, this one. Is there any evidence that this is the correct

explanation?

The aim of this paper is to bring together the various lines of experimental evidence bearing upon this question, which have come to light as the result of fourteen years of continuous work in my laboratory on this problem. In this work there have taken part more than *forty* investigators, and each of these has worked on his problem from *one to five years*, making a total of from 75 to 100 years' work for one man. The more important of this evidence will now be briefly discussed.

# I. RELATION BETWEEN LOWERING OF FREEZING-POINT AND WATER OF CRYSTALLIZATION.

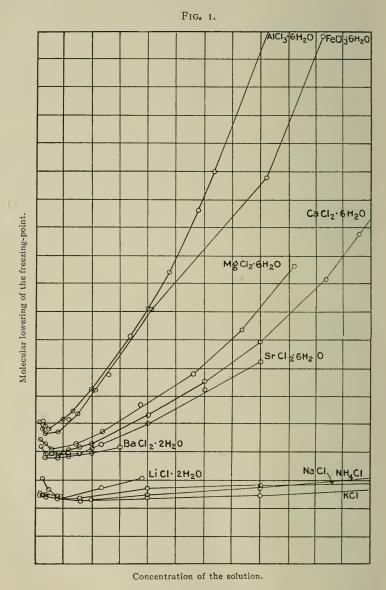
The work of Jones and Getman <sup>7</sup> brought out a relation between lowering of freezing-point and water of crystallization. They worked with a large number of chlorides, bromides, iodides, and nitrates, measuring the freezing-point lowerings produced by solutions of these substances of known concentrations; and, from the lowerings found experimentally, calculated the corresponding molecular lowerings. They then compared with one another the molecular lowerings produced by the various chlorides. Similarly, the molecular lowerings produced by the various bromides and iodides. Finally, the molecular lowerings produced by a large number of nitrates were compared. The result was the discovery of the relation between the magnitude of the freezing-point lowering produced by the different substances, and the amounts of water with which these substances crystallized under the same conditions from aqueous solution.

This relation can be best seen from the following figures taken from the work of Jones and Getman.<sup>8</sup>

<sup>&</sup>lt;sup>7</sup> Zeit. phys. Chem., 46, 244 (1903); Phys. Rev., 18, 146 (1904); Amer. Chem. Jour., 31, 303 (1904); Carneg. Inst. of Washington, Publication No. 60.

<sup>8</sup> Zeit. phys. Chem., 49, 433 (1904); Journ. Chem. Phys., 3, 478 (1905).

The freezing-point lowerings produced by the following chlorides were measured: sodium, potassium, ammonium, lithium,



barium, strontium, calcium, magnesium, iron, and aluminium. From the freezing-point lowerings found experimentally, the

molecular lowerings were calculated for a number of concentrations. The molecular lowerings as ordinates were plotted against the molecular lowerings as ordinates were plotted against the concentrations as abscissæ. The curves are shown in Fig. 1.

The chlorides of sodium, potassium, and ammonium, which crystallize without water, fall at the bottom of the sheet. Then comes the chloride of lithium with two molecules of water. Barium chloride, with two molecules of water, is considerably above the chloride of lithium, but barium chloride is a ternary electrolyte, yielding three ions, while lithium chloride is binary,

The chlorides of calcium, strontium, and magnesium, each crystallizing with six molecules of water, give curves which fall nearly together, and are much higher on the curve sheet than the chlorides which crystallize without water.

We finally come to the quarternary chlorides of aluminium and iron, which crystallize with six molecules of water each. These give much greater molecular lowerings than the ternary chlorides with the same amount of water of crystallization. The molecular lowerings of the freezing-point, then, produced by the various chlorides, are a function of the amounts of water with which these salts crystallize. But molecular lowering of the freezing-point is an expression of the amount of water which the salt holds in combination in solution. Therefore, the amount of water with which the chlorides are in combination in solution, is a function of the amount which the chloride is capable of bringing with it out of solution as water of crystallization.

The bromides of cadmium, potassium, sodium, lithium, barium, strontium, calcium, and magnesium were studied in an exactly similar manner, and the results plotted as curves. These substances fall in the same order on the curve sheet as the amounts of water with which they crystallize.

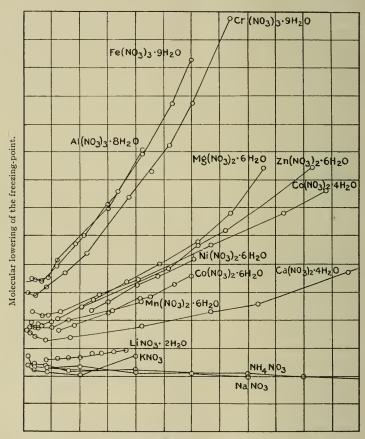
The iodides were similarly studied. These included the iodides of cadmium, potassium, sodium, lithium, barium, strontium, and calcium. The iodide curve-sheet brings out the relation between water of crystallization and water of hydration, just as satisfactorily as the chloride and the bromide sheet.

The nitrates as a class are very soluble salts. For this reason a large number of these substances were studied, and the results obtained plotted as curves. The nitrate sheet (Fig. 2) includes the nitrates of sodium, ammonium, potassium, lithium, calcium,

manganese, cobalt, nickel, cadmium, zinc, magnesium, iron, chromium, and aluminium.

The nitrates of sodium, ammonium, and potassium, which crystallize without water, fall at the bottom of the sheet. The last point in the curve for potassium nitrate is an error in plotting the

FIG. 2.



Concentration of the solution.

curve. This curve practically coincides with the curves for sodium and ammonium nitrates. Lithium nitrate, with two molecules of water of crystallization, falls a little above the curves for the other alkaline nitrates. Calcium nitrate is especially interesting. It crystallizes with four molecules of water, and falls below the

curves for the salts with six molecules of water. It will be recalled that calcium chloride, like the chlorides of strontium and magnesium, crystallizes with six molecules of water, and its freezing-point curve is practically coincident with those of the other alkaline earth chlorides. The nitrate of calcium, crystallizing with four molecules of water, would, in terms of the relation we are now studying, be expected to fall below the nitrates with six molecules of water, and such is the fact. This compound alone adds special interest to the nitrate sheet.

The nitrates of manganese, cobalt, nickel, zinc, and magnesium, each crystallizing with six molecules of water, give freezing-point curves which fall very close together, and which are higher on the sheet, showing greater lowering of the freezing-point than the curve for calcium nitrate.

Finally, we come to the quarternary chlorides of iron, aluminium, and chromium. These crystallize with eight and nine molecules of water. They lower the freezing-point of water more than any other known nitrates. Indeed, their freezing-point lowering is from four to five times as great as would be calculated on the assumption that there is no combination between the solvent and the dissolved substance. The same is true of the chlorides of these elements.

We have compared above the salts of the same acid with different metals. Relations of interest and importance manifest themselves between the salts of the same metal with different acids.

Chlorides, bromides, iodides, and nitrates crystallizing without water all give a molecular lowering of between 3 and 4. This increases very slightly with increase in concentration. Lithium chloride, with two molecules of water of crystallization, gives about the same freezing-point lowering as lithium nitrate with two molecules of water, and less lowering than lithium bromide or iodide, with three molecules of water each. The bromide and iodide give about the same freezing-point lowering.

Sodium bromide and iodide each crystallizes with two molecules of water, and they produce very nearly the same lowering of the freezing-point.

Barium chloride, bromide, and iodide all crystallize with two molecules of water. Since barium chloride is only slightly soluble, the comparison must be limited to dilute solutions. Here all

Vol. CLXXVI, No. 1055-35

three salts show about the same lowering of the freezing-point of water. In the more concentrated solutions the iodide shows greater lowering than the bromide. If we compare the chlorides, bromides, and iodides of the alkaline earths, they all crystallize with six molecules of water, and they produce lowerings of the freezing-point of the same order of magnitude. The bromides give slightly greater lowerings than the chlorides, and the iodides than the bromides.

The nitrates give just about the same lowerings as the corresponding chlorides, and, therefore, slightly less than the bromides and iodides.

The nitrates of iron and aluminium, with nine and eight molecules of water of crystallization, give greater lowerings than the corresponding chlorides which crystallize with six molecules of water each.

Thus, the relation between water of crystallization and lowering of freezing-point comes out on every hand, whether we compare the salts of a given acid with different metals, or the salts of the same metal with different acids.

A study of all of the data obtained by Jones and Getman seemed to justify the conclusion that "Those substances which crystallize with the largest number of molecules of water of crystallization, give the greatest molecular lowering of the freezing-point of water in concentrated solutions."

The number of compounds studied by Jones and Getman was sufficiently large to show that the above relation is a general one. It is obvious that this relation is a fundamental one. Those substances which combine with the largest amounts of water out of solution, water of crystallization, would be the ones which would form the more complex hydrates in solution. These would be the compounds which would produce the greatest lowering of the freezing-point of water, and, consequently, the greatest molecular lowering: since the water which is combined with the dissolved substance as water of hydration is removed from the field of action, so far as solvent is concerned. Having established the relation between lowering of freezing-point and water of crystallization, Jones and Getman calculated the composition of the hydrates formed by a number of substances at various dilutions. To do this, it was necessary to know the molecular lowering of the freezing-point at the dilution in question, the molecular lowering calculated from the dissociation at the same dilution; and the amount of water present in a given volume of the solution.

Jones and Getman <sup>9</sup> found that the composition of the hydrates formed by a given substance at various dilutions, increased with the dilution, as would be expected from the law of mass action. They found also that the total amount of water combined with the dissolved substances increased with the concentration of the solution, and plotted curves expressing the relation between total amount of water in combination and the concentrations of the solutions. These curves were found to be perfectly regular for all of the substances investigated. This is also what would be expected from the law of mass action. This was all regarded as good preliminary evidence, at least, that there is combination between the dissolved substance and the water.

## 2. RELATION BETWEEN WATER OF CRYSTALLIZATION AND TEM-PERATURE OF CRYSTALLIZATION.

Another consequence of the hydrate theory of solution is the following: It is a general fact that rise in temperature decreases the complexity of complexes. Hydrates are no exception to this relation. It is a very simple matter to remove from a saturated solution all of the water except that with which the salt crystallizes. It is only necessary to maintain it at its boiling-point for a sufficient length of time. The hydrate in solution under such conditions must have approximately the same composition as the salt with its water of crystallization. This same salt was shown from our work to form hydrates in more dilute solutions and at lower temperature, which are many times more complex than the salt with crystal water. Thus, calcium chloride crystallizes with six molecules of water of crystallization. It was found that a molecule of calcium chloride in more dilute solution and at lower temperatures can combine with at least thirty molecules of water. 10 These facts all show that the hydrates are relatively unstable, breaking down with rise in temperature.

Since a salt holds less water in combination with it the higher the temperature to which the solution is heated, it would seem to

<sup>&</sup>lt;sup>o</sup> Zeit. phys. Chem., 49, 447 (1904).

<sup>&</sup>lt;sup>10</sup> Either the molecule or the resulting ions can combine with this amount of water.

follow that a salt should bring with it out of solution less and less water the higher the temperature at which it crystallizes. In a word, a salt should have less and less water of crystallization the higher the temperature at which it crystallizes.

That this was in general true was a well-known fact. We were, however, surprised on examining the literature to find how general this relation is, and what wide differences in water of crystallization manifested themselves for such a large number of substances.

A few examples taken from the work of Jones and Bassett <sup>11</sup> well illustrate this point. Take the chlorides of magnesium, iron, and manganese, and the nitrates of nickel and cobalt. The number of molecules of water of crystallization and the temperatures of crystallization are given:

Salt with number of molecules	·
of water of crystallization	Temperature of crystallization
MgCl <sub>2</sub> .6H <sub>2</sub> O	10° to 12° ·
MgCl <sub>2</sub> .12H <sub>2</sub> O	+ 20°
MgCl <sub>2</sub> .10H <sub>2</sub> O	above + 20°
MgCl <sub>2</sub> .8H <sub>2</sub> O	Higher temperatures.
FeCl <sub>2</sub> .6H <sub>2</sub> O	— 16° to + 20°
FeCl <sub>3</sub> .3½H <sub>2</sub> O	+ 20°
FeCl <sub>3</sub> .2½H <sub>2</sub> O	+ 40° to + 60°
FeCl <sub>2</sub> .2H <sub>2</sub> O	+ 60° to + 80°
FeCl <sub>2</sub> .oH <sub>2</sub> O	+80° and above.
1 0013.01120	i co ana assve.
MnCl <sub>2</sub> .12H <sub>2</sub> O	— 48°
MnCl <sub>2</sub> .11H <sub>2</sub> O	$-21^{\circ}$ to $-37^{\circ}$
MnCl <sub>2</sub> .6H <sub>2</sub> O	—21°
MnCl <sub>2</sub> .4H <sub>2</sub> O	+ 15°
MnCl <sub>2</sub> .2H <sub>2</sub> O	+ 20°
(	0
Ni(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O	- 27°
Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	— 16°
Ni(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O	+ 58° and higher.
CO(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O	—29° to —22°
CO(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	$-22^{\circ}$ to $+56^{\circ}$
CO(NO <sub>3</sub> ) <sub>2.3</sub> H <sub>2</sub> O	+ 56° to + 91°
, , , ,	
Cu(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O	— 20° to — 24°
Cu(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	o° to — 10°
$Cu(NO_3)_2.3H_2O$	Ordinary temperatures.

<sup>&</sup>lt;sup>11</sup> Zeit. phys. Chem., 52, 1231 (1905).

Calcium chloride crystallizes with the following amounts of water as the temperature of crystallization is lower and lower:

Salt with number of molecules of water of crystallization Temperature of crystallization  $CaCl_2.6H_2O$ ;  $CaCl_2.4H_2O$ ; CaCl2.2H2O; CaCl2.H2O; Mg(NO<sub>3</sub>)<sub>2.9</sub>H<sub>2</sub>O — 17° Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O + 18° Higher temperatures. Mg(NO<sub>3</sub>)<sub>2.2</sub>H<sub>2</sub>O  $0^{\circ}$  to  $+6^{\circ}$ MnSO<sub>4.7</sub>H<sub>2</sub>O MnSO<sub>4.5</sub>H<sub>2</sub>O  $+15^{\circ}$  to  $+20^{\circ}$ MnSO<sub>4.4</sub>H<sub>2</sub>O  $+25^{\circ}$  to  $+31^{\circ}$ MnSO<sub>4.3</sub>H<sub>2</sub>O — 10° to — 18° A1Brs.15H2O A1Bra.6H2O At ordinary temperature. A1I3.15H2O At ordinary temperature. A113.6H2O

A large number of examples were found illustrating this same point, but those given above will suffice to show how regularly water of crystallization decreases with rise in temperature. This relation seems to be a perfectly general one. So far as is known to the writer, there is not a single exception to this general relation.

Jones and Bassett carried out some preliminary experiments, which made it probable that some well-known compounds can be made to crystallize with still larger amounts of water than had hitherto been supposed to be possible, by crystallizing them at very low temperatures. The general relation between water of crystallization and temperature of crystallization is, then, just what would be expected from the solvate theory of solution. The higher the temperature the simpler the hydrates existing in aqueous solution. The higher the temperature of crystallization the simpler the hydrates which separate as water of crystallization when the salt crystallizes out of the solution. This is all in keeping with the hydrate theory of solution, and can be regarded as evidence for it. Indeed, it is difficult to see how hydrates (salts with water of crystallization) could separate out of solution if they did not exist in solution. It is almost inconceivable that a salt would combine with water on leaving the solution as crystals, and hold that water in fairly stable combination as water of crystallization; and would not combine with even more water when in solution in that solvent,—i.e., when in the presence of a large excess of water. The law of mass action would almost force us to this conclusion.

However this may be, the direct line of evidence referred to above is the point upon which it is desired here to lay stress.

## 3. MINIMA IN THE BOILING-POINT CURVES.

An examination of Figs. 1 and 2 will show that practically all of the curves pass through a well-defined minimum. The minima in the freezing-point curves are for very dilute solutions. Let us see just what these minima mean. With increasing dilution the molecular lowerings of the freezing-point increase, due to increasing dissociation. This causes the curves to rise as the dilution is increased. With increasing concentration the curves would continue to fall, did not hydration take place. Hydration removes more and more water from the field of action as solvent. and, consequently, the remaining smaller and smaller amount of water with increasing concentration has its freezing-point lowered more and more. Therefore, the molecular lowering increases more and more the greater the concentration of the solution. This would tend to make the freezing-point curves rise with the concentration. The minimum in a freezing-point curve is, therefore, the point where these two conditions just equalize one another. Starting with the most concentrated solution and proceeding towards the more dilute, we have the curve approaching the abscissæ, due to the total amount of combined water becoming less and less as the dilution becomes greater and greater. With increasing dilution, however, the dissociation becomes greater and greater, and this would cause the freezing-point curve to rise. Where these two opposite influences are just equal to one another in effect, we have the minimum in the curve. On the more dilute side of the minimum, the effect of increasing dissociation more than overcomes the opposite effect of decreasing hydration and the curve rises. On the more concentrated side of the minimum, the effect of increasing amount of combined water more than overcomes the opposite effect of decreasing dissociation, and the curve rises here also; whence the minimum. With this explanation in mind of the nature of the minimum in the freezing-point curves, we can now understand another line of evidence bearing on the solvate theory.

Jones and Getman, 12 having furnished the evidence already discussed in connection with the relation between lowering of freezing-point and water of crystallization; and having calculated the composition of the hydrates formed by a large number of

<sup>12</sup> Amer. Chem. Journ., 32, 338 (1904).

substances at various dilutions in water as the solvent, turned to various solvents to see what evidence could be obtained as to whether solvents other than water combined with substances dissolved in them. They studied certain salts in ethyl alcohol, not measuring their lowering of the freezing-point, since this would be impossible on account of the low temperature at which alcohol freezes; but the rise in the boiling-point. Boiling-point curves were obtained in which the molecular rise in the boiling-point were plotted against concentrations of the solutions. Minima were also found in the boiling-point curves, but these were at greater concentrations than the minima in the freezing-point curves. Let us see just what this means. The minima in the freezing-point curves were the points at which decreasing hydration with increasing dilution, tending to make the curve fall, was just offset by increasing dissociation which made the curve rise.

Just so it is with the boiling-point curves. Here, however, where the temperature was higher the hydration was less; since, as we have seen, hydrates are more and more unstable the higher the temperature to which they are heated. It would, therefore, require at the boiling-point of the solution, greater concentration to secure the necessary hydration, in order that this effect might overcome the opposite effect of dissociation. We should, therefore, expect to find the minimum in the boiling-point curves at a greater concentration than in the freezing-point curves, and such is the fact.

This was brought out by the work of Jones and Getman already referred to; and also by that of Jones and McMaster <sup>13</sup> along the same general line.

These and other investigations in this laboratory showed that solvents other than water do combine with at least certain substances dissolved in them, and that we have not simply hydration in aqueous solutions, but alcoholation in the alcohols. Other work, which will be referred to later, has shown that glycerol also combines with more or less of the dissolved substance, and that we have glycerolation as well as alcoholation. Similar work in acetone shows that this solvent combines with more or less of the dissolved substance, as we shall see. We thus have not simply a theory of hydration in aqueous solutions, but of solvation in solvents in general. The hydrate theory thus becomes the solvate theory of solution.

<sup>13</sup> Amer. Chem. Journ., 35, 316 (1906).

The important point in the present connection is that the minimum in the boiling-point curves, being at greater concentration than in the freezing-point curve, is in keeping with the solvate theory. Indeed, it could have been predicted from the theory before a single fact was established experimentally, and is, therefore, regarded as evidence in favor of the theory.

# 4. HYDRATING POWER AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY.

The conductivities of solutions of electrolytes are a function of two things: The number of the ions and the velocities with which they move. The conductivities of solutions increase in general, with rise in temperature. This must, therefore, be due either to an increase in the number of ions present, or to an increase in the velocity of the ions. It has been shown beyond question that rise in temperature does not increase the number of ions present. Indeed, the effect of rising temperature is to diminish the number of ions present—to diminish the dissociation.

The increase in conductivity with rise in temperature must, then, be due to an increase in the velocity with which the ions move. This can be brought about in a number of ways. The ions may move faster with rise in temperature, due to a diminution in the viscosity of the solvent which always takes place as the temperature rises. The magnitude of this change in viscosity with rising temperature has been worked out in this laboratory not only for water, but for a large number of nonaqueous solvents.14 It has been found that the increase in conductivity with rise in temperature, is due largely to a breaking down of the complex hydrates as the temperature rises. Starting with this fact, certain relations of interest and importance between the temperature coefficients of conductivity and the magnitude of the hydration have been discovered. These relations were first pointed out from the theory of solvation, and then verified by the experimental facts.

That the complex hydrates break down with rise in temperature has been shown beyond question. The higher the temperature the less complex the hydrate existing around the ion. The less complex the hydrate attached to the ion, the less the mass of the ion, and the less its resistance when moving through the

<sup>&</sup>lt;sup>14</sup> See Publications of the Carnegie Institution of Washington, Nos. 80 and 180. <sup>15</sup> Amer. Chem. Journ., 35, 445 (1906).

solvent. If this decreasing complexity of the hydrate about the ion has any pronounced effect in determining the magnitude of the temperature coefficients of conductivity, then the following deductions from the solvate theory were made, as necessary conclusions from this theory, before a single experimental fact was examined to see whether the conclusions were verified.

It would seem reasonable to suppose that the more complex the hydrate about any ion, the greater would be the change in the complexity of the hydrate as the temperature is raised. The larger the number of molecules of water combined with an ion, the larger the number that could, and probably would be split off with rise in temperature. In a word, from the solvate theory those ions with the greatest hydrating power would be the ones that would be expected to have the greatest temperature coefficients of conductivity; since the temperature coefficients of conductivity are determined largely by the decrease in the complexity of the hydrate with rise in temperature. This is one conclusion from the solvate theory in connection with the temperature coefficients of conductivity.

If different ions have approximately equal hydrating power, we should expect the change in the complexity of these hydrates to be of about the same order of magnitude. Therefore, ions with approximately equal hydrating power, should have temperature coefficients of conductivity of the same order of magnitude. This conclusion can also be tested by the experimental facts.

The hydrates existing in solution have been shown by Jones and his co-workers to be more complex the more dilute the solution. The hydrates being more complex in the more dilute solutions, the change in the composition of the hydrates with rise in temperature would be greater in the more dilute solutions. Therefore, we should expect that the temperature coefficients of conductivity would be greater the more dilute the solution studied. This conclusion, like the two foregoing, can be tested by the results of experiment.

One other conclusion is of interest and importance: The higher the temperature the more unstable the hydrate. We should therefore expect the breaking down of the complex hydrates into simpler hydrates, to take place more rapidly at the higher temperatures. The result would be that the temperature coefficients of conductivity would be larger the higher the temperature. This conclusion can also be tested by the experimental facts.

The following data are taken from the work of this laboratory, published by the Carnegie Institution of Washington; Monograph No. 170, page 77:

#### TABLE I.

	Temperature coefficients in conductivity units.			
Substances with slight hydrating power.		0 35° = 1024	v=8.v=	
Sodium chloride	2.00	2.46	2.27	2.82
Sodium bromide	1.89		2.18	2.79
Sodium iodide	2.12	2.54	2.33	3.14
Sodium nitrate	2.04	2.45	2.02	2.67
Sodium chlorate	1.77	2,22	2.15	2.90
Potassium chloride	2.39	2.84	2.45	3.11
Potassium bromide	2.43	2.91	2.45	3.11
Potassium iodide	2.38	2.91	2.65	3.37
Potassium nitrate	2.08	2.16	2.31	2.83
Potassium chlorate	2.02	2.52	2.23	2.94
Potassium permanganate	2.04	2.31	2.29	2.23
Potassium sulphocyanate	2.20	2.56	2.34	
Ammonium chloride	2.42	2.94	2.51	3.69
Ammonium bromide	2.32	2.86	2,58	3.11
Ammonium nitrate	2.17	2.50	2.33	3.04

#### TABLE II.

		Temperature coefficients in conductivity units.		
Substances with large hydrating power.		to 35° = 1024	v = 8.v	o 65° = 1024
Calcium chloride	3.49	4.85		
Calcium bromide	3.73	5.00	4.03	6.03
Calcium nitrate	3.09	4.79	3.33	
Strontium chloride	. 3.37	5.13	3.92	6.02
Strontium bromide	3.66	5.27	4.08	
Strontium nitrate	2.76	4.86	3.58	
Barium nitrate	3.09	4.74	3.34	• • •
Magnesium chloride	3.40	4.72	3.61	
Magnesium bromide	. 3.55	4.44	4.08	
Magnesium nitrate	3.10	4.78	3.57	
Zinc nitrate	3.13	4.47	3.43	5.41
Manganous chloride	. 3.14	4.86	3.43	6.37
Nickel chloride	3.41	5.04	3.61	
Nickel nitrate	3.21	4.58		
Cobalt chloride	3.39	4.95	3.54	
Cobalt bromide	3.32	4.96	3.75	
Cobalt nitrate	3.20	4.67	3.05	
Cupric nitrate	3.18	4.88		
Aluminium chloride	. 4.57	8.64	5.16	12.49
Aluminium nitrate	4.19	7.86	4.87	11.65

These facts suffice to test the above conclusions from the hydrate theory. The compounds in Table I have slight hydrating power, as would be expected from the fact that they crystallize with little water of crystallization, or with no water at all. Those in Table II all crystallize with large amounts of water, although with different amounts of water. These substances are all strongly hydrated.

The substances in Table I have much smaller temperature coefficients of conductivity at all temperatures and dilutions than those in Table II. This is true even taking into account the fact that the substances in Table I are all binary electrolytes; while those in Table II are in general ternary; the chloride and nitrate

of aluminium being quarternary electrolytes.

The second conclusion can also be tested by comparing Tables I and II. The substances in Table I all have slight hydrating power,—*i.c.*, they all have hydrating power of the same order of magnitude. Their temperature coefficients of conductivity are all of the same order of magnitude.

Those in Table II have very great hydrating power, yet all have hydrating power of approximately the same order of magnitude. This would be expected from the fact that most of these substances crystallize with six molecules of water. The temperature coefficients of conductivity of most of the substances in Table II are of the same order of magnitude. Aluminium chloride crystallizes with six molecules of water, and aluminium nitrate with eight. These are quarternary electrolytes and have, therefore, larger temperature coefficients of conductivity.

The third point, that temperature coefficients of conductivity are greater at the higher dilution, can also be tested by the above facts. A comparison of the temperature coefficients in both tables, —i.e., for those substances which hydrate very little and those which hydrate largely,—will show the larger coefficients for the higher dilutions.

The fourth and last conclusion, that the temperature coefficients should be greater the higher the temperature, is also borne out by the experimental results.

To summarize the four conclusions from the solvate theory, which are substantiated by the experimental facts, we have:

1. The temperature coefficients of conductivity are larger the greater the hydrating power of the salt.

- 2. The temperature coefficients of conductivity for substances having approximately the same hydrating power are approximately the same.
- 3. The temperature coefficients of conductivity increase with the dilution of the solution, being greatest for those salts with large hydrating power.

4. The temperature coefficients of conductivity increase with the temperature; the increase being greatest for those substances

with large hydrating power.

The conclusions from the solvate theory are thus confirmed by the facts at every point, so far as the temperature coefficients of conductivity are concerned. The number of these deductions is so large, and the confirmations so satisfactory and convincing, that this is regarded as very strong evidence in favor of the general correctness of the theory of solvation in solution. Without this theory it seems impossible to explain a single one of the above relations.

The following co-workers have investigated this phase of the problem: West, <sup>16</sup> Jacobson, <sup>17</sup> White, <sup>18</sup> Clover, <sup>19</sup> Wightman, <sup>20</sup> Hosford, <sup>21</sup> Winston, <sup>22</sup> Kreider, <sup>23</sup> Springer, <sup>24</sup> Howard, <sup>25</sup> Shaeffer, <sup>26</sup> and Smith. <sup>27</sup>

This work has all been published as a monograph,<sup>28</sup> by the Carnegie Institution of Washington.

# 5. DISSOCIATION AS MEASURED BY THE FREEZING-POINT METHOD AND BY THE CONDUCTIVITY METHOD.

The water that is combined with the molecules, or the ions resulting from the dissociation of the molecules, is removed from

```
    Amer. Chem. Journ., 34, 357 (1905); 44, 508 (1910).
    Ibid., 40, 355 (1908).
    Ibid., 42, 520 (1909); 44, 135 (1910).
    Ibid., 43, 187 (1910).
```

<sup>&</sup>lt;sup>20</sup> *Ibid.*, 46, 56 (1911); 48, 320 (1912).

<sup>&</sup>lt;sup>21</sup> *Ibid.*, 46, 240 (1911). <sup>22</sup> *Ibid.*, 46, 368 (1911).

<sup>&</sup>lt;sup>23</sup> Carnegie Institution of Washington, Publication No. 170.

<sup>&</sup>lt;sup>24</sup> Amer. Chem. Journ., 48, 411 (1912).

<sup>&</sup>lt;sup>25</sup> *Ibid.*, 48, 501 (1912).

<sup>&</sup>lt;sup>26</sup> Ibid., 49, 207 (1913).

<sup>&</sup>lt;sup>27</sup> Ibid., 50, 1 (1913).

<sup>&</sup>lt;sup>28</sup> Carnegie Institution of Washington, Publication No. 170.

the field of action so far as solvent is concerned. This, as we have seen, affects the freezing-point lowering directly. The lowering of the freezing-point of a solvent by a given amount of a dissolved substance, depends upon the ratio between the number of parts of the substance and solvent. The part of the liquid present not acting as solvent plays no part in the freezing-point lowering. Therefore, the freezing-point lowering shown is much greater than if there was no hydration; and greater, just in proportion to the amount of solvent combined with the substance as water of hydration.

If half of the water were combined as water of hydration, the freezing-point lowering of the remaining half would be just double what it would be if there were no hydration. If two-thirds of the water present were in a state of combination, the freezing-point lowering would be three times that of an unhydrated substance, and so on. The dissociation calculated from the abnormally great freezing-point lowering would, of course, be abnormally large. In a word, freezing-point lowering would be affected almost

lineally by hydration.

The dissociation of electrolytes as measured by the conductivity method depends upon two factors, the number of the ions in a given volume of the solution and the velocities with which they move. The hydrated ions would move slower than the unhydrated, having a greater mass. The number of the ions would probably not be greatly affected by the hydration. It would seem, therefore, that hydration would have less effect on dissociation as measured by the conductivity method than as measured by the freezing-point method. We predicted, before trying a single experiment, that dissociation as measured by the freezing-point method would be greater than as measured by the conductivity method. Dr. J. N. Pearce 29 took up in my laboratory a fairly elaborate investigation of this point. He measured the dissociations of calcium, strontium, magnesium, and barium chlorides; the nitrates of calcium, strontium, magnesium, and barium; cobalt chloride and nitrate; copper chloride and nitrate; nickel nitrate; aluminium chloride; sodium bromide; hydrochloric, nitric, and sulphuric acids; -over as wide range of dilution as the freezing-point method could be used. The nature of the results obtained can be seen from the following data, taken from the paper by Jones and Pearce:

<sup>20</sup> Amer. Chem. Journ., 38, 411 (1907).

Salt.	Concentration.	Dissociation from conductivity.	Dissociation from freezing-point lowering.
	( 0.01	89.67	90.61
CaCl <sub>2</sub>	0.05	80.62	80.96
	(0.10	74.35	76.35
	( 0.10	75.65	78.83
BaCl <sub>2</sub>	{ 0.10	80.09	85.19
	( 0.01	90.87	96.85
MgCl <sub>2</sub>	( 0.01	73.61	87.68
	\ 0.05	79.78	90.97
	( 0.01	90.90	97.10
SrCl <sub>2</sub>	( 0.10	74.17	84.46
	\ 0.05	78.08	82.65
	10.0	89.37	91.87
	{ 0.01 0.05	61.36	62.95
Ba(NO <sub>3</sub> ) <sub>2</sub>	{ 0.05	70.47	75.18
	( 0.01	86.37	99.06
	{ 0.075 0.05	76.57	81.32
Ni(NO <sub>3</sub> ) <sub>2</sub>	₹ 0.05	79.83	83.72
	( 0.01	91.10	98.03
	( 0.01	76.48	85.48
$Co(NO_3)_2 \dots$	< 0.05	81.73	88.26
	10.0	92.40	98.65

Solutions much more concentrated than the above were also studied, but on account of the hydration it was impossible to determine their dissociation by the freezing-point method. Hence, the comparisons were made at the above dilutions.

An examination of the above data will show that the dissociation as measured by the freezing-point method is greater than as measured by conductivity. This was found almost invariably to be the case. The prediction from the solvate theory was thus fully confirmed by the experimentally established facts. This is regarded as evidence in favor of the theory from which the prediction was made.

One other point bearing upon the solvate theory of solution came out in this work of Pearce, which is interesting and probably important: The freezing-point data for the most concentrated solutions were used as the basis for calculating the composition of the hydrates present in the solutions. It was found that the hydrating power of a salt is primarily a function of the cation.

The relation in question is between the atomic volumes of the elements and their power to form hydrates. If the atomic volumes are plotted as ordinates and the atomic weights as abscissæ, we have the well-known atomic volume curve, which brings out a periodic relation. Potassium, rubidium, and cæsium fall at the highest maxima. Salts of these elements crystallize without water. Lithium and sodium also fall at maxima on this curve, but at much lower maxima. The salts of these elements crystallize with two and three molecules of water, and show in solution some hydrating power. The atomic volumes of lithium and sodium are smaller than those of potassium, rubidium, and cæsium.

At the minimum in the third division of the atomic volume curve we find strontium, iron, cobalt, nickel, and copper. Salts of these elements crystallize with large amounts of water, and these salts when in solution show large hydrating power. Aluminium with about half the atomic weight of iron, has a slightly larger atomic volume, falling at the second minimum of the curve. Its salts crystallize with eight and nine molecules of water, and show the very greatest hydrating power in solution.

Of the calcium group, barium has the largest atomic volume and the smallest hydrating power; strontium, with a larger atomic volume than calcium, has a smaller hydrating power than calcium; while magnesium has the smallest atomic volume of this group, and the greatest hydrating power. An examination of all the data available shows that the hydrating power of the cation is an inverse function of its atomic volume. The question arises, What does this mean? what is its physical significance? The smaller the ion, probably the greater the electrical density of the charge upon it. The power of the ion to combine with the solvent seems to be a function of the electrical density of the charge upon the ion.

### 6. HYDRATING POWER OF THE IONS AND THEIR VELOCITIES.

Another relation that was brought out by the work of Pearce, has proved useful in explaining certain apparent discrepancies which presented themselves in the relative velocities with which the ions move. It is well known that the velocities of the ions are an inverse function of their mass and probably, also, a function of their volumes. We should expect those ions with the

smallest atomic volumes to have the greatest velocities. We frequently find the opposite. Potassium, rubidium, and cæsium, with the exception of hydrogen and hydroxyl, have the highest velocities; while the elements of the iron and copper group, which have very small atomic volumes, have the smallest migration velocities.

If we study the two curves representing the relation between atomic volumes and atomic weights, and between migration velocities and atomic weights, it shows at once the cause of this apparent anomaly. It has been shown that those elements which have the smallest atomic volumes have the greatest hydrating power, and vice versa. We see, then, that those ions which have the smallest migration velocities have also the greatest hydrating power.

A somewhat detailed comparison of the members of the dif-

ferent groups will bring out this idea more clearly.

The atomic volumes of potassium, rubidium, and cæsium increase rapidly with increasing atomic weights, and, as a rule, their salts crystallize without water. We should expect, then, the potassium ion to have the greatest migration velocity, and the cæsium ion to have the smallest. Experiments show that they have approximately the same migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have migration velocities which are only about two-thirds that of potassium. It will be remembered that sodium and lithium form salts which may crystallize with two and three molecules of water, respectively. Hence, we may assume that the increase in volume of the sodium and lithium ions, due to the formation of a relatively large hydrate, decreases the velocity of those ions to a far greater extent than the slight hydration of the large potassium ion decreases the velocity of that ion.

The atomic volume of lithium is about one-half that of sodium, and the maximum amount of water with which lithium salts crystallize from solution is three molecules, whereas the maximum for sodium salts is two molecules. Since the ratio of 2:3 represents approximately the ratio of the hydrating power of the two ions in solution, we should expect the effect upon the velocity, of the greater increase in the volume of the small lithium ion, due to its hydration, to compensate somewhat for the smaller increase in the volume of the larger sodium ion. Experiment shows that the migration velocities are nearly equal.

The same relation holds for the metals of the alkaline earth group. The atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts crystallize with six molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with two molecules of water, or water-free. On the other hand, the magnesium cation, which has one-half the atomic volume of the calcium ion, has nearly the same migration velocity, due to compensation between the atomic volumes and the hydration of the ions.

The calcium ion has a slightly greater atomic volume than sodium, yet, owing to its much greater hydrating power, its migration velocity is considerably less.

The cations of copper, cobalt, and nickel have nearly the same atomic volumes and the same hydrating power. We should expect them to have the same migration velocity, and such is the case.

The atomic volumes of the halogens, chlorine, bromine, and iodine, are approximately the same. If their ions are hydrated we should expect them to combine with the same amount of water, and, therefore, they should give migration velocities of the same order of magnitude. This has been found to be the case. The atomic volume of fluorine has not been determined, but from its position on the migration velocity curve we should infer that its atomic volume is smaller than that of the halogens, and that its ion possesses a considerable degree of hydrating power.

Further, it will be noted that the migration velocities of the halogens are almost identical with those of the alkalies standing next above them in order of atomic weights, whereas their atomic volumes are very much smaller. This leads us to believe that the compensation, which brings about an equalization of the migration velocities of the two groups, is due to the increase in volume of the alkali ions by hydration.

The silver ion alone of all the metallic elements for which satisfactory data can be found presents an exception. It has a small atomic volume, and its salts crystallize from solution without water. We should expect it to have but slight hydrating power in solution, and it should, therefore, have a high migration velocity; but this has been found to be slightly less than that of the halogens.

# 7. ACTION OF A SALT WITH HYDRATING POWER ON ANOTHER SALT IN THE SAME SOLUTION.

Jones and Stine <sup>36</sup> studied the action of a salt with hydrating power on the complexity of the hydrates formed by another salt present in the same solution. The pairs of salts investigated are potassium chloride and calcium chloride, calcium chloride and magnesium chloride, calcium chloride and strontium chloride, magnesium nitrate and strontium nitrate, magnesium nitrate and calcium nitrate, aluminium chloride and ferric chloride, calcium chloride and calcium nitrate, sodium bromide and lithium bromide. and a pair of salts which form only the simplest hydrates—potassium chloride and ammonium chloride. The problem consisted in calculating the approximate composition of the hydrates which are formed by the two substances when they are simultaneously present in the solution. It is obvious that the difficulties are much greater in this case than simply to calculate the approximate composition of the hydrates formed when this is only one substance present in the solution.

By taking into account, experimentally and theoretically, all of the many factors involved, considerable light was, however, thrown on this problem. The action of one salt with a common ion on the conductivity of a second salt was calculated from the law of mass action. We developed the formula for calculating the relation between freezing-point lowering and hydration if only one salt formed hydrates; and also the formula when both salts form hydrates.

The salts were obviously so chosen as to give us the opportunity to study a great variety of conditions. The first two have a common anion, and only one has any appreciable hydrating power. One of these salts is a binary, and the other a ternary electrolyte. The next four pairs are ternary electrolytes with a common anion; and both of the members of each of these pairs have large hydrating power. The next two salts are quarternary electrolytes with a common anion, and both have great hydrating power. The next two have a common cation. The last pair but one has a common anion, and both salts show considerable hydrating power; while the two members of the last pair have a common cation, and neither shows any considerable hydrating power.

<sup>80</sup> Amer. Chem. Journ., 39, 313 (1908).

It was found that when two hydrated salts are mixed each dehydrates the other to some extent, the amount being controlled by the law of mass action. This would be the case only if the calculated composition of the hydrates was approximately correct.

It was further shown that the ions and molecules have very different hydrating power. While in most cases the ions have the greater hydrating power, in some special cases the molecules seem to have the greater power to combine with water.

Some interesting results were obtained when potassium chloride and ammonium chloride were mixed; both of these salts having only slight hydrating power. If two salts with a common ion are mixed, each drives back the conductivity of the other, and it has been assumed that this is due almost entirely to a suppression of the dissociation. If this were the complete explanation, we would have the greatest effect on the conductivity when the salts in question were most strongly dissociated. Since the dissociation at zero degrees is greater than at 25°, the diminution in the conductivity should be greater at the lower temperature.

The fact is exactly the opposite. There is a very small suppression of the ionization at zero, a more marked action at 12°; and at 25° there is a very pronounced difference between the conductivity of the mixture and the sum of the conductivities of the constituents. It is therefore obvious that the suppression of the ionization is not the only factor which comes into play here. This is made perfectly obvious by the fact that a number of the above-named solutions are practically isohydric.

Other factors which can come into play are:

The change in the viscosity of the solution produced by mixing the two salts. The change in the size and mass of the ionic spheres, due to the change in the hydration caused by mixing the two salts.

The action of one salt on the other present in the same solution is, thus, not as simple as was assumed, there being several factors coming into play. For details of this work see Publication of the Carnegie Institution of Washington, No. 180.

### 8. WORK IN MIXED SOLVENTS.

The work in mixed solvents, including water, methyl alcohol, ethyl alcohol, acetone, and glycerol, and mixtures of these solvents with one another, has been in progress in this laboratory contin-

uously for a dozen years. This work has been carried out by my co-operators, Lindsay,<sup>31</sup> Carroll,<sup>32</sup> Bingham,<sup>33</sup> Bassett,<sup>34</sup> Rouiller,<sup>35</sup> McMaster,<sup>36</sup> Veazey,<sup>37</sup> Kreider,<sup>38</sup> Mahin,<sup>39</sup> Schmidt,<sup>40</sup> Guy,<sup>41</sup> and Davis.<sup>42</sup> This work has been published collectively by the Carnegie Institution of Washington.<sup>43</sup> A fairly large number of salts were investigated in the pure and in the mixed solvents, and results were obtained which bear directly upon the solvate theory of solution.

The conductivity of a salt like potassium iodide in mixtures of methyl alcohol and water has, in a particular mixture of these two solvents, a decided minimum. The significance of this minimum was satisfactorily explained by Jones and Murray. They studied the effect of one associated solvent on the association of another associated solvent in the following manner. They determined the molecular weight of acetic acid dissolved in formic acid, changing the dilution of the acetic acid. These are both associated solvents, and neither appreciably dissociates the other. They found that the molecular weight decreases rapidly as the dilution of the solution increases. This shows that formic acid diminishes the association of acetic acid.

They then performed the converse experiment, using acetic acid as the solvent and dissolving formic acid in it, changing the dilution of the formic acid present. They found that the molecular weight of the formic acid became less and less as the dilution of the solution became greater and greater, showing that the acetic acid was breaking down the association of the formic acid. Thus, each of these two solvents breaks down the association of the other.

Then, water and acetic acid were studied in a similar manner.

```
31 Amer. Chem. Journ., 28, 329 (1902).
32 Ibid., 32, 521 (1904).
33 Ibid., 34, 481 (1905).
34 Ibid., 32, 409 (1904).
35 Ibid., 36, 440 (1906).
36 Ibid., 36, 325 (1906).
37 Zeit. phys. Chem., 61, 641 (1908); 62, 44 (1908).
38 Amer. Chem. Journ., 45, 282 (1911).
39 Ibid., 41, 433 (1909); Zeit. phys. Chem., 69, 389 (1909).
40 Amer. Chem. Journ., 42, 37 (1909).
41 Ibid., 46, 131 (1911).
42 Zeit. phys. Chem., 81, 68 (1912).
```

<sup>&</sup>lt;sup>43</sup> Carnegie Institution of Washington, Publications Nos. 80 and 180. <sup>44</sup> Amer. Chem. Journ., 30, 193 (1903).

Water dissociates acetic acid only slightly. It was found that each of these solvents breaks down the association of the other; similarly, water and formic acid each breaks down the association of the other. Jones and Murray conclude from this work that associated solvents in general diminish each other's association. Indeed, this is what common-sense would suggest as highly probable. An associated solvent, as is well known, breaks down the molecules of dissolved electrolytes into their ions. Similarly, an associated solvent breaks down the molecules of nonelectrolytes dissolved in it, not into ions, since that is not possible, but into the simplest molecules. Since each of the two associated solvents diminishes the association of the other, each diminishes the dissociating power of the other, in terms of the well-known relation between the association of a solvent and its dissociating power. Consequently, two associated solvents, such as water and methyl alcohol, when mixed, possess less dissociating power than would be calculated from the composition of the mixture and the law of averages. A substance dissolved in a mixture of two associated solvents will show a conductivity minimum in that particular mixture in which each solvent lowers the association of the other to the greatest extent; or at least, the sum of the two lowerings of the association is a maximum. This also explains why it is that a salt dissolved in a mixture of water and methyl alcohol may have in the proper mixtures a smaller molecular conductivity than in the pure methyl alcohol alone. Each solvent diminishes the association of the other, and, consequently, its dissociating power. When acetone was used as one of the solvents the minimum did not appear, but a pronounced maximum in the conductivity curve manifested itself. The maximum was very pronounced when lithium nitrate or calcium nitrate was used, and when a mixture of acetone with methyl or ethyl alcohol was employed as the solvent. It was shown theoretically that this maximum must have one of two causes: It must be due either to an increase in the dissociation increasing the number of ions present; or to a diminution in the size of the ionic spheres, accelerating the velocity of the ions. It is easy to eliminate one of these factors. The direct measurement of the dissociation in mixtures of the above-named solvents shows that such mixtures do not dissociate to a greater extent than would be calculated from the dissociating powers of the individual solvents. Having excluded this factor, we are forced to conclude that the conductivity maximum is caused

by a change in the solvation of the ion, or the amount of the solvent with which the ion is combined.

In dealing with the conductivity in pure solvents, as well as in the mixtures of these with one another, we must therefore take into account the magnitude of the spheres of the solvent surrounding the ions, and especially any changes in the magnitudes of these spheres in the different mixtures of the solvents. Every change in the magnitude of these spheres would produce a change in the effective masses of the ions, and, consequently, a change in the velocities with which they move.

.The magnitude of the ionic spheres is an important factor in conditioning the conductivity, and changes in the magnitudes of these spheres in the different mixtures of the solvents are the most important factor in producing the maximum in the conductivity curves. The maximum occurs in that mixture where the ionic spheres are a minimum. This seems to be the only possible explanation of the maximum. The relation of the solvate theory to the temperature coefficients of conductivity in nonaqueous and in mixed solvents, is just as important as the relation between hydration and the temperature coefficients of conductivity in aqueous solutions. Since these relations have already been fully discussed for aqueous solutions, the discussion will not be repeated for nonaqueous solutions. For this reference must be had to the Carnegie Publications above referred to.<sup>45</sup>

Evidence was furnished by the work of Schmidt, Guy and Davis,<sup>45</sup> that glycerol also has the power to combine to some extent with certain substances dissolved in it. It would, however, lead us too far here to discuss this in any detail. Here, again, reference only can be made to the collective publications of these researches.

One other fact was discovered by Jones and McMaster, working in mixed solvents, to which brief reference will be made. It was found that certain salts in certain mixtures of certain solvents have negative temperature coefficients of conductivity. This is true of cobalt chloride in the 75 per cent. mixture of acetone with methyl alcohol; and also in the 50 and 75 per cent. mixtures of acetone with ethyl alcohol. Negative temperature coefficients of conductivity had been observed at low temperatures; but this seems to have been the first time that they were observed at ordinary temperatures. What do they mean?

<sup>&</sup>lt;sup>45</sup> Publications Carnegie Institution of Washington, Nos. 80 and 180.

With rise in temperature the solvent becomes less viscous, increasing the velocity of the ions. With rise in temperature the association of the solvent becomes less, and, consequently, its dissociating power; which means that at the higher temperature there would be a smaller number of ions present in the solution. These two influences act counter to one another, the former increasing the conductivity and the latter diminishing it. When the temperature coefficient of conductivity is negative, it means that the decrease in the number of ions with rise in temperature more than counterbalances the effect on conductivity of the increased velocity with which the ions move. This explanation accounts very satisfactorily for the results in nonaqueous solvents. The alcohols and acetone are, at ordinary temperatures, highly associated liquids. Rise in temperature diminishes their association, and, consequently, their dissociating power.

Jones and McMaster found that a solution of cobalt chloride, v = 200, in a mixture of 75 per cent. acetone with methyl alcohol has a zero temperature coefficient of conductivity. It was found that in nonaqueous solvents, as well as in water, certain salts, especially those of potassium, rubidium, and cæsium, lower the viscosity of the solvent in which they are dissolved. Jones and Veazey explained this fact in the same way that they did the corresponding fact in water. If the ionic volume of the dissolved ion is much larger than the molecular volume of the solvent molecules, the effect would be to diminish the frictional surfaces that would come in contact, and consequently to diminish the friction when the molecules move over one another.

It is well known that potassium, rubidium, and cæsium occupy the maxima on the atomic volume curve. Here, again, for details reference must be had to the Publications of the Carnegie Institution of Washington, Nos. 80 and 180.

9. EVIDENCE FOR SOLVATION BASED UPON THE POWER OF SOLUTIONS TO ABSORB LIGHT.  $^{46}$ 

A brief account of some of our work on the absorption spectra of solutions has already been published in this journal.<sup>47</sup> This

<sup>&</sup>lt;sup>40</sup> All of the work herein described on the absorption spectra of solutions, and a large amount which cannot even be here referred to, have been carried out with the aid of grants from the Carnegie Institution of Washington to H. C. Jones. (See Publications of the Carnegie Institution of Washington, Nos. 60, 110, 130, 160, and 190.)

<sup>&</sup>lt;sup>47</sup> Journal of The Franklin Institute, 173, 228 (1912).

was, however, far too brief to give any adequate conception of the work done or the results obtained. It may not at first sight seem obvious how a study of the power of solutions to absorb light could bear on the solvate theory of solution. A moment's thought will show how this is the case.

The absorption of light by substances in solution is a resonance phenomenon. Something in the solution must be thrown into resonance by any given wave-length of light, in order that that wave-length may be stopped. If an ether vibration of given wave-length finds something in the solution which it can set vibrating, the energy in that particular wave-length is expended in setting up the new vibration, or the light of this wave-length is, as we say, absorbed. If all of the wave-lengths of light find something which they can throw into resonance with themselves. they are all stopped, or the solution is, as we say, opaque. If none of the wave-lengths of light find anything in the solution which they can throw into resonance, none of them are stopped, or the solution is, as we say, transparent. Resonance causes opacity; the lack of resonance, transparency. The color of solutions is, then, due to the fact that certain wave-lengths of light are absorbed by the solution, while others pass on through. Those that pass on through give the color to the solution in question. The thing in the solution which is thrown into resonance by the ether vibrations impinging upon it is called the resonator. It was supposed until recently that this was the ion, which is a charged atom or group of atoms. Since the atom has been shown by Thomson to be a complex system; and since he has shown in what its complexity consists, viz., electrical charges, we have about come to the conclusion that it is these electrical charges or electrons which are the resonators or absorbers of light. However this may be, the fact pointed out above is true; that the absorption of light by dissolved substances is due to a resonator in the solution being thrown into resonance with the wave-lengths of light that are absorbed. This resonator, whatever it is, would probably have different resonance when anhydrous than when combined with more or less of the solvent; and, further, the resonance would be different when different amounts of the solvent were combined with the resonator.

We can now see how a study of the absorption spectra of solutions could throw light on the nature of solution. The anhydrous

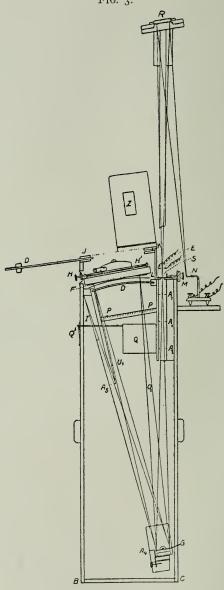
resonator should have different absorption from the hydrated resonator. If we vary the amount of water in combination with the resonator we should change the absorption spectra of the solution. There are, as we shall see, a number of ways of doing this, and marked changes in the absorption spectra have resulted. Further, when a salt is dissolved in a given solvent, it combines with some of that solvent. In water we have hydrates; in alcohol we have alcoholates; in glycerol, glycerolates, etc., we should expect the resonator to be affected differently by the different kinds of solvates around it. In a word, we should expect a salt dissolved in different solvents to have different absorption spectra. We shall learn that such is the case.

## IO. WORK OF JONES AND UHLER.

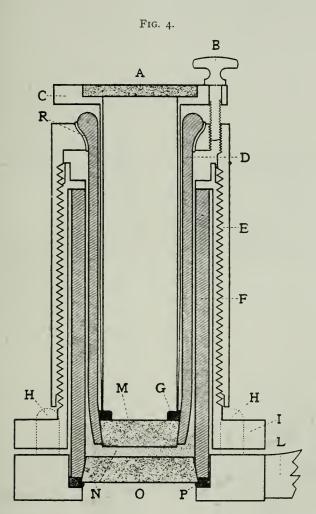
Work on the absorption spectra of solutions has been in progress in this laboratory continuously for eight years, under grants from the Carnegie Institution of Washington. The experimental work at first consisted in allowing white light from a Nernst glower to pass through a solution, then fall on a concave grating, and then upon a photographic plate. The wave-lengths that were absorbed by the solution would appear as dark lines or bands upon the photographic plate. About eight thousand solutions have already been studied. The apparatus used by Jones and Uhler,48 who first worked on absorption spectra, is shown in Fig. 3, which is one-fifth the natural size. Light from the Nernst glower, N, is concentrated on the slit S by the concave mirror R. It then passes to the Rowland grating G. From this a part of the light is sent to the photographic film F. The slit-width is regulated by the micrometer screw M.  $Q_1$  and  $Q_2$  are screens. If  $Q_2$  is perpendicular the light passes directly to the film. If  $Q_1$ is horizontal, only ultraviolet light of wave-length shorter than 0.4  $\mu$  reaches the film. H and  $H_1$  are a toothed-wheel system for moving non-exposed parts of the plate successively into the path of the light from the grating. Q and  $Q_1$  are doors leading into the spectroscope. Several black diaphragms and screens,  $A_1$ ,  $A_2$ ,  $A_3$ , etc., protect the photographic film from all spectra with the exception of that which is desired.  $U_1$  and  $O_1$  are the extreme rays of the spectrum of the first order, which can be investigated.

<sup>48</sup> Amer. Chem. Journ., 37, 138 (1907).





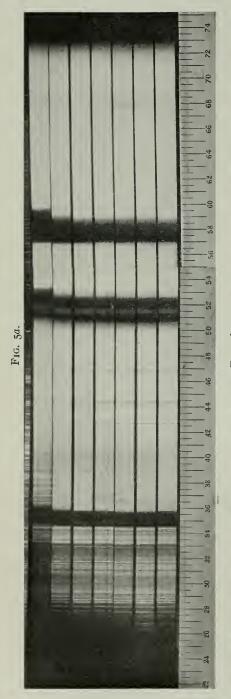
Jones and Uhler constructed a number of forms of cells for this work. They will not be described here in detail. Suffice it to say here that they were provided with quartz ends so as to transmit the ultraviolet light. A cell was devised for non-aqueous solutions <sup>48</sup> which was free from all cement. The principle consisted in this; that conical pieces of quartz were carefully

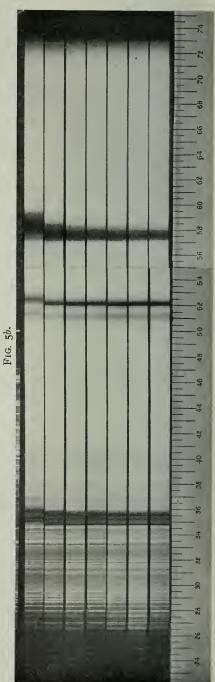


ground into the ends of glass tubes and held in position by suitable mechanical arrangements.

A vertical section of the cell, enlarged to twice the natural

<sup>48</sup> Amer. Chem. Journ., 34, 246 (1907).





I j

size, is shown by Fig. 5, and the details of the several parts may be explained as follows: In its fundamental principles, the cell consisted of three distinct parts: (a) An outer glass tube with a quartz bottom to hold the liquid; (b) an inner glass tube with a quartz plate at the lower end to regulate the depth of the liquid, and to cause the upper surface of the absorbing layer of solution to be both plane and parallel to the quartz bottom of the larger glass tube; (c) a mechanism which would act as a stopper to the system of glass and quartz just mentioned, and which would also enable the experimenter to adjust the cell for any desired depth of absorbing layer from zero to the full capacity of the cell,—i.e., about 3.5 cm.

The separate parts of this piece of apparatus will be described in the order in which they would be assembled for actual use. M denotes a plane parallel plate of quartz, ground carefully in the form of a frustum of a cone, so as to fit very accurately into the conical hole at the lower end of the glass tube D. The thickness of this quartz plate was 4.6 mm., and its least diameter was 12.6 mm. The glass tube was blown with a thick shoulder at its upper end. The plate M was first slipped into place in the tube D, and then the rubber washer B was pushed down against the quartz by introducing the brass tube C into the glass tube. In order to prevent dust from entering the inner tubes, the plane parallel quartz plate A was permanently set into a cylindrical depression in the upper end of the glass tube C. This plate was 2 mm. thick and 20 mm. in diameter.

The brass tube widened out into a sort of plate at its upper end, and this projection was pierced by three holes at the vertices of an equilateral triangle. Through these holes suitable screws passed, and one of these is shown at B, Fig. 4. After the brass tube C had been introduced into the glass tube, the washer R, made of blotting-paper, was slipped up over the outside of the glass tube, until it would not pass through the shoulder of this tube. Then the group of parts thus far described was let down through the hole at the upper end of the hollow brass cylinder E, as far as it could go,—i.e., until the washer R was tightly squeezed between the glass and brass surfaces. The three screws were next pushed through their respective holes, and turned until the quartz plate M was forced, liquid-tight, into the conical hole in the glass tube; care being taken at the same time to so adjust the system as to

have the axis of rotation of the glass tube and quartz plate parallel to the axis of the brass cylinder E. A thread of convenient pitch had been accurately cut in the inner surface of this cylinder. The purpose of this thread, as well as that of a fine line or groove which had been turned on the outside of the cylinder, in a plane at right angles to the axis of the latter, will be explained below.

Whenever the cell had been entirely taken apart, which was not often necessary, the distance between the plane of the lower surface of the quartz plate M, and the plane of the lower end of the cylinder E, had to be measured and recorded, since this distance varied with the thickness of the two washers and with the pressure exerted by the screws. The number expressing this distance was one of several numbers that had to be known in order to adjust the cell for a given depth.

The thread at E was next fitted to the thread that had been accurately cut to fit it on the outside of the brass cylinder *I*. Then the two cylinders were screwed together until the distance between the fine cut around the outside of E, and a certain point of the upper plane surface of the flange at the bottom of the cylinder I, had the proper value. This distance was, of course, measured along a generating line of the outer surface at E and, therefore, perpendicular to the plane just located. The assemblage of parts explained above formed a complete system in itself, and comprised all of parts L and C, using the notation of the remarks introductory to the more detailed discussion of the cell. The flange at the bottom of I was provided with three large and two small holes, and all of them pierced it parallel to the axis of the cylinder. The larger holes fitted closely over three pillars, H and H, while the smaller ones corresponded to two little screws. The pillars and screws were not in the plane of the diagram. The object of the pillars and screws will be explained a little later. The cylinder I was also turned so as to have a collar on its interior near the top.

When the desired depth of absorbing liquid had been determined upon the basis of intensity of color, etc., the distance between the line around E and the upper plane of the flange of I was found by the addition of three numbers. One of these was a constant of the apparatus, 1.34 cm., and the other two expressed, respectively, the required depth of solution, and the distance from the lower plane surface of the quartz plates M to the plane of the

lower end of the brass cylinder E. As an example from practice, for a depth of 2 cm. the sum was 1.34 + 2.00 + 0.69 = 4.03 cm.,—
i.e., the two cylinders E and I had to be screwed around each other until the line to the flange was equal to 4.03 cm.

Conversely, knowing this distance as well as the two cell data,

Conversely, knowing this distance as well as the two cell data, it was merely a matter of algebraic addition to obtain the effective

depth of the cell.

The remaining parts of the apparatus had the characteristics described below, and were assembled as follows: L denotes the handle of a stout, hollow, cylindrical plate, which formed the bottom of the complete cell. The interior of this plate was turned out so as to leave a flange at the bottom upon which the rubber washer P was placed. The three pillars mentioned above projected vertically from, and were rigidly attached to the plate L. Two holes had been tapped out of this plate to correspond accurately to the smooth holes of the flange of I. After laying the washer P, on the flange of L, and after pushing and turning the quartz plate M tight up into the conical holes of the glass tube F, the transparent system was set vertically with its lower end resting symmetrically on the washer. The thickness and the smallest diameter of this quartz plate were, respectively, 4.6 mm. and 19 mm. The solution to be studied, N, was next poured into the vessel constituted by F and O. It was necessary to measure the depth of the liquid, and it was found convenient to make this depth 2 mm. greater than the effective depth of the cell.

The assembled system of parts A, B, C, D, G, I, M, R was next let down over the glass tube F, until the upper flange inside the cylinder I rested on top of this tube. The three pillars H guided the system into the correct position, and prevented any rotation of the cylinders I and L around each other. Lastly, the two little screws were passed through the holes in the lower rim of I, and the two cylinders were screwed tightly together. This operation completed the adjustment of the cell. It is seen at once, from the preceding explanation, that the liquid or solution in question came only in contact with glass and quartz surfaces; while the vapor of the solutions studied did not act on brass, glass and quartz, and since the apparatus did not leak, the cell gave entire satisfaction. For vapors which would attack brass, but not the silicates, it is easy to see how a system could be designed which would differ from the one just described in

having coaxial glass tubes dip into a trap of some neutral liquid, instead of the brass cylinders E and I. Moreover, it would be quite possible to design the parts of the cell in such a way as to impart to the liquid the shape of a wedge or prism of adjustable angle and depth.

The work of Jones and Uhler had to do with three classes of facts, as we shall see. They studied the effect on the absorption, of increasing the concentration of the solution. They found that with increasing concentration of the solution the absorption bands widened. With increasing concentration of solutions of cobalt chloride, the absorption in the ultraviolet widened. The absorption bands in the green also became broader. Similarly, the ultraviolet absorption of copper chloride became broader with increasing concentration; and also the bands in the red. The bands of copper bromide also became broader with increasing concentration.

In interpreting the spectrograms, we must take into account the difference between the observed broadening of the absorption bands, and the broadening which would theoretically result if a change in concentration produced only an increase in the number of absorbing parts per unit volume, and not an increase in their active mass. The well-known theoretical formula, expressing the law of Beer and Lambert, is  $J = J\hat{o}adc$ , where d is the thickness of the absorbing layer and c the concentration. To test this law, it is necessary to vary the depth of the layer of the solution, in the same way and to the same extent as the dilution is varied. Jones and Uhler also studied the effect on absorption spectra of adding a dehydrating agent in the form of a second salt. The result was a widening of the bands. The absorption bands of cobalt chloride in the ultraviolet and green became wider as the amount of calcium chloride added increased. In this work the amount of cobalt chloride was kept constant, while the mass of the dehydrating agent was varied. The same result was obtained with cobalt chloride and copper chloride, to which increasing amounts of aluminium chloride were added.

The third point tested by Jones and Uhler was the effect of the addition of water to solutions in nonaqueous solvents. Thus, to solutions of salts in methyl alcohol, ethyl alcohol and acetone, different amounts of water were added, and the corresponding spectrograms photographed. The action of water was to narrow the absorption bands.

These facts were all interpreted in terms of the solvate theory of solution. Since, however, so much more direct evidence for the theory has been furnished by subsequent experimental work, these results will not be discussed in any detail.

## II. WORK OF JONES AND ANDERSON ON THE ABSORPTION SPECTRA OF SOLUTIONS.

The second investigation in this laboratory on the absorption spectra of solutions was carried out by Jones and Anderson. They used essentially the same apparatus that had been employed by Jones and Uhler, enlarging the spectroscope so as to extend from  $\lambda_{2000}$  to  $\lambda_{7600}$ . The Nernst glower was employed for wavelengths longer than  $\lambda_{3200}$ , and a spark for the shorter wavelengths. It was necessary to have a spark with a very large number of lines, but without any lines of very great intensity. Carbon terminals, saturated with ammonium molybdate and uranium nitrate, gave the desired result.

Jones and Anderson worked in terms of Beer's law with solutions of salts of cobalt, nickel, copper, iron, chromium, neodymium, praseodymium, and erbium. In all they studied about 1200 solutions.

The salts of cobalt show one region of absorption in the ultraviolet and one in the green. The bands in the ultraviolet narrow with dilution in all cases where the conditions of Beer's law are fulfilled. It, however, remains constant when the molecules are kept constant. This would indicate that the absorber or resonator here is attached to, or is a part of the undissociated molecule, or the undissociated molecule itself. The bands near \(\lambda\_{3300}\) quickly disappear as the dilution is increased, even if the molecules in the path of the beam of light are kept constant. Its intensity increases rapidly with rising temperature. These bands cannot, therefore, be produced by molecules, but are probably due to relatively simple hydrates. Rise in temperature causes the complex hydrates to decompose into relatively simple hydrates, thus increasing the intensity of the band. Increase in the dilution increases the complexity of the hydrates, and thus causes the band to disappear. These facts all point to the conclusion that the band is due to relatively simple hydrates.

<sup>\*\*</sup> Carnegie Institution of Washington, Publication No. 110. Amer. Chem. Journ., 41, 163, 276 (1909).

Vol. CLXXVI, No. 1055-37

The green cobalt bands appear in all aqueous solutions of cobalt salts, yet with different intensities. If these bands were due to the cobalt ions, they would have the greatest intensities in those solutions which are most strongly dissociated,—i.e., in the most dilute solutions; the product of concentration times depth of layer being kept constant. For twice normal solutions the cobalt salts arrange themselves in the following order with respect to the increasing intensity of the green bands; nitrate, bromide, chloride, sulphocyanate. For one-tenth to two-tenths normal solution the sequence is; bromide, chloride, nitrate, sulphate, acetate, sulphocyanate. The order of their increasing dissociation is: acetate, sulphate, sulphocyanate, nitrate, chloride, bromide—which is almost the reverse of the above. This band, therefore, cannot be due to the cobalt ion. We found, however, that if the concentration of the sulphate is varied from 0.55 to 0.60 normal, which would change very little the dissociation, and the light passed through depths of layer of the solution such that the product of depth times concentration is a constant, the breadth of the green cobalt band does not change. This shows that the absorption producing this band is simply proportional to the number of cobalt atoms in the solution, regardless of their hydration. The green cobalt bands are therefore due to the cobalt atoms; the intensity of the absorption depends, however, on what these atoms are combined with. Aqueous solutions of cobalt salts absorb very little in the red, if they are not concentrated, or if they are hot. The presence of red absorption in solutions of medium concentration shows that this is not due to the ions. That there is red absorption in very concentrated solutions, would lead us to suspect that it was due to molecular aggregates. since the absorption in the red increases with rising temperature, and since molecular aggregates are broken down with rise in temperature, it follows that these aggregates are not the cause of the red absorption of cobalt salts. The conditions which cause the red absorption,—high concentration, high temperature, and presence of a dehydrating agent,—are the conditions which give rise to simple hydrates. That the absorption in the red depends on simple hydrates is made more probable by the following facts: All the anhydrous salts show absorption in the red, being blue; likewise, the salts with only a few molecules of water; while the salts with six molecules of water show no red absorption.

The chloride and bromide of cobalt were studied in methyl alcohol, ethyl alcohol, and acetone. The chloride, which in water has an absorption band at  $\lambda_{3300}$ , in the alcohols has two bands,  $\lambda_{3100}$  and  $\lambda_{3600}$ . These bands quickly disappear with dilution, and resemble in their general properties the  $\lambda_{3300}$  band in aqueous solutions. These bands have their origin in simple solvates. The green cobalt band is present in the nonaqueous solutions studied. This is what we would expect if it was due to the cobalt atom.

The absorption in the red is stronger in nonaqueous than in aqueous solutions, and the intensity increases in the following order: Methyl alcohol, ethyl alcohol, acetone. With increase in dilution the bands quickly narrow in methyl alcohol, more slowly in ethyl alcohol, and they remain almost constant in ace-This cannot be explained on the ground of dissociation, but can easily be explained on the assumption of simple solvates; since the power to form solvates decreases in the order methyl alcohol, ethyl alcohol, acetone. In methyl alcohol we have the most complex solvate, and, consequently, the least intense absorption bands. We thus see that the absorption spectra of cobalt salts are complex, the different absorption bands being due to different causes. The ultraviolet bands are due to simple hydrates, the green bands to the cobalt atom, and the absorption in the red also to simple hydrates. The absorption bands of nickel salts behave like the green cobalt bands. The nickel chloride band  $\lambda_{3060}$  shows a decided widening as we approach a saturated solution. It also widens on the addition of large amounts of calcium chloride or aluminium chloride. From our study of the green cobalt bands we concluded that it was due to the cobalt atom. We must conclude that the absorption bands of nickel are due chiefly to the nickel atom.

The absorption spectrum of copper salts is much simpler than that of cobalt, consisting of only three absorption bands. We will consider only the bands in the ultraviolet and in the red. The absorption in the ultraviolet decreases rapidly with the dilution, the product of concentration and depth of layer of the solution being kept constant. Therefore, this band cannot be due to ions, but must be due to molecules. It should be observed that the absorption decreases with the dilution even when the entire number of molecules in the path of the beam of light is kept constant. This shows that the absorbing power of a molecule is markedly

affected by its immediate surroundings. It might be assumed that this was due to the formation of molecular aggregates. That this is not the case, is shown by the fact that a rise in temperature has the same effect on this band as increasing the concentration of the solution. It is well known that molecular aggregates are broken down by rise in temperature, and this would cause a decrease instead of an increase in the absorption. On the other hand, increase in concentration would increase the magnitude of these aggregates; but this produces the same change in the absorption bands as rise in temperature. The magnitude of the solvation, on the contrary, is diminished both by increase in concentration and rise in temperature. We must therefore conclude that the ultraviolet absorption of copper salts depends upon the solvated molecules, and that the absorbing power of these molecules is less the more complex the solvates.

It should be stated that the absorption in the ultraviolet in aqueous solutions is smallest, and increases if we pass from methyl alcohol to ethyl alcohol. The change in the absorption with dilution is greatest in aqueous solutions, and decreases if we pass from methyl alcohol to ethyl alcohol. This is what we should expect, since the solvating power is greatest in water, and decreases from methyl alcohol to ethyl alcohol. Therefore, the solvates would become less complex as we proceed from water to methyl alcohol, to ethyl alcohol. Consequently, with change in dilution, there should be greater change in the composition of the solvates in the aqueous solutions than in solutions in methyl or ethyl alcohol, and such is the fact.

The red absorption bands of copper become somewhat narrower when the product of concentration and thickness of absorbing layer is kept constant, but broaden somewhat when the molecules are kept constant. Their intensity changes much less with the solvent than the intensity of the violet bands. We conclude that these bands, like the green cobalt bands, are due to the metal atom, whose absorbing power is affected only slightly by its immediate surroundings.

The behavior of the red copper bands in methyl alcohol, on adding water, is remarkable. The bands at first broaden, and then, when more water is added, decrease in breadth. When a small amount of water is added, simple hydrates are formed. On the addition of more water these would become more com-

plex. The absorption of light by the relatively simple hydrates formed when a small amount of water is added, is greater than the methyl alcoholates existing in the solution in methyl alcohol; therefore, the first action of the water is to broaden the bands. The subsequent narrowing of the bands on the further addition of water is due to the more complex hydrates formed under these conditions. Similarly, ethyl alcohol narrows the bands, as would be expected; since here the solvates are simpler than in methyl alcohol.

The most important and interesting results obtained by Jones and Anderson have to do with salts of neodymium and praseodymium. It was found that the chloride and bromide of neodymium, in aqueous solutions of all concentrations, give practically identical spectra. The spectrum of the nitrate differs considerably from that of the chloride and bromide, especially in concentrated solution. For every band in the solution of the chloride there is a corresponding band in the solution of the nitrate; but in the more concentrated solutions the bands have a very different appearance. The nitrate bands are much broader and more washed out than those of the chloride, but with increasing dilution they become similar to the chloride bands. That the dilute solutions of the different salts of neodymium would have similar absorption bands would be expected from the theory of electrolytic dissociation; but this theory can in no wise explain the behavior of the nitrate bands.

Our work on the absorption spectra of neodymium chloride in mixtures of alcohol and water, makes it very probable that the molecules as well as the ions of this salt undergo solvation in solution. This enables us to explain the results with the chloride, bromide, and nitrate, if we assume that the absorption bands, in the ultimate analysis, are due to electrons which exist in the neodymium atom, or are intimately connected with it. If the atoms are free, the electrons will respond to certain wave-lengths of light. If the atoms are combined with three chlorine atoms as in neodymium chloride, these chlorine atoms would affect the periods of the neodymium electrons, and, consequently, the absorbing power of the neodymium atom. If we dissolve a neodymium salt in a solvent which would have no direct action on the salt, but would allow its molecules free movement, we would not expect that the solvent would have any appreciable influence on the light-

absorbing power of the neodymium atom. On the other hand, a solvent like water, which forms complex hydrates with the salt, could exercise a very marked influence on the absorption spectra of the salt; and this effect would be greater the more complex the anion of the salt. Take a salt like neodymium chloride (NdCl<sub>3</sub>), where there are only three foreign atoms to affect the periods of the neodymium electrons. If this salt were combined with ten molecules of water of hydration, then there would be 30 atoms of the solvent affecting the neodymium electrons within the neodymium atom. If we were dealing with the nitrate Nd(NO)<sub>3</sub>, we would have 12 foreign atoms in addition to the 30 of water of hydration; and 12 to 30 is much greater than 3 to 30. This would lead us to suspect that the spectrum of the nitrate in concentrated solution would be very different from that of the chloride or bromide.

If we increase the dilution of the solution, all of the above salts will dissociate into neodymium cations which cause the absorption and the corresponding anions. The cation is combined with ten molecules of water, no matter from which neodymium salt it comes. The anions, now being separated from the cation, have little or no effect on the periods of the electrons in the neodymium system. The change produced by dissociation of the molecule in the entire number of atoms which affect the periods of the neodymium electrons, is greatest for the salt with the most complex anion. Therefore, those salts whose molecules consist of the largest number of atoms combined with the neodymium atom, as the nitrate, sulphate, and acetate, on dissociating, should show the greatest change in their absorption spectra. Such is the fact. The spectrum of the nitrate changes with the dilution far more than that of the chloride or bromide. theory also explains why the spectra of all three salts in very dilute solutions, where they are practically completely dissociated, are practically the same.

The most important point brought out by the work of Jones and Anderson is the following: A salt like neodymium chloride has a very different absorption spectrum in water from what it has in methyl alcohol. (See Fig. 5.) If such a salt is dissolved in a mixture of alcohol and water, and the relative amounts of water varied from 100 per cent. to 15 or 20 per cent., no change is observed. If the water relative to the alcohol is still further

diminished, the resulting spectrum is a superposition of the spectra of the aqueous solution and of the alcoholic solution. The spectrum of the aqueous solution decreases in intensity as the amount of water present decreases, and at the same time the alcoholic spectrum increases in intensity. The exact composition of the mixed solvent, in which both of the spectra have the same intensity, depends somewhat on the concentration of the salt.

In general, it is from 7 to 8 per cent. water.

The results that were obtained for neodymium chloride in methyl alcohol and in mixtures of methyl alcohol and water are shown in Fig. 5. The uppermost strip of a corresponds to a solution of neodymium chloride in pure methyl alcohol. The second strip corresponds to a solution of neodymium chloride of the same concentration in methyl alcohol containing  $16\frac{2}{3}$  per cent. of water. It will be seen that the absorption is very different in the pure alcohol from what it is in the mixed solvents. Succeeding strips correspond to the addition of more and more water. Strip 3 from the top corresponds to  $33\frac{1}{3}$  per cent. water, strip 4 to 50 per cent. water, strip 5 to  $66\frac{2}{3}$  per cent. water, strip 6 to  $83\frac{1}{3}$  per cent. water, and strip 7 to pure water.

It will be seen that the entire change in the absorption spectrum takes place on the addition of 16% per cent. of water to the methyl alcohol, and that the absorption in water is quite different

from in alcohol.

In order to determine whether there was simply a shift in the position of the alcohol bands on the addition of water, or whether there were really new absorption bands in the water, b, Fig. 5, was taken. In this case a much more dilute solution of neodymium chloride was used. In the uppermost strip we have again the salt dissolved in the pure alcohol. In the second strip we have the salt in a mixture of methyl alcohol and  $16\frac{2}{3}$  per cent. of water, and in the succeeding strips more and more water is present. A comparison of the uppermost strip with strip 2 will show that in the two cases we are dealing with very different absorption bands. The number and structure of the bands in the pure alcohol are very different from the bands when there is water present. In a word, the "water bands" are not the "alcohol bands" simply shifted in position, but entirely different absorption bands.

We have here, then, a well-defined "alcohol" spectrum and

a well-defined "water" spectrum of neodymium chloride, just as we predicted from the solvate theory should exist.

The addition of more than  $16\frac{2}{3}$  per cent. of water to the alcohol does not further change the absorption spectrum in the case of the more dilute, as in the case of the more concentrated solution of neodymium chloride.

So far as is known to me, this is the first case ever found of the effect of a nonabsorbing solvent on the absorption spectrum of a compound dissolved in it—of the existence of well-defined "solvent bands."

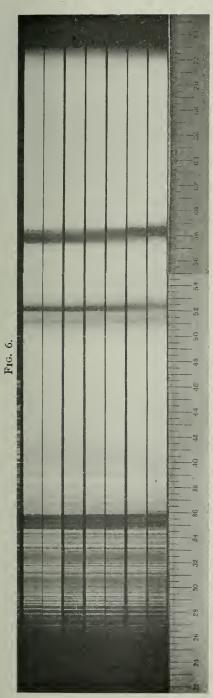
Having found that all of the change in the absorption spectrum was produced on adding 16% per cent. of water, we determined to study this change in detail by adding very small and increasing amounts of water to the alcohol.

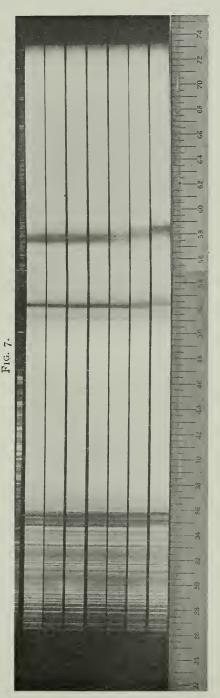
Fig. 6 represents the results obtained when neodymium chloride was dissolved in a mixture of methyl alcohol and water. The concentration of the neodymium chloride was constant = 0.5 normal. The percentages of water, beginning with the solution whose spectrum is adjacent to the numbered scale, were 0, 5.5, 10.6, 16, 21.3, 26.6, and 32. The depth of the solution throughout was 0.5 cm.

In the second strip the bands characteristic of the alcohol solution are much more prominent than those belonging to the aqueous solution, while in the third strip the reverse is true. This shows that the composition of the mixed solvent which gives the bands with about half their normal intensity is 7 to 8 per cent. water. There we have both the "alcohol" and the "water" bands coexisting, and they are seen to have very different structures—are very different bands. The "water" bands decrease in intensity as the amount of water present decreases.

Take next, solutions in mixtures of methyl alcohol and water. The results are shown in Fig. 7, the concentration of the neodymium chloride being 0.15 normal.

The strip next to the numbered scale corresponds to the pure alcohol. As we go away from the scale the strips correspond to more and more water. In strip 3, counting from the bottom, which corresponds to 5.3 per cent. of water, we have both the "water" and the "alcohol" bands of equal intensity. As we go up the spectrogram, corresponding to the presence of more and more water, the "water" bands become stronger and stronger and the alcohol bands weaker, and quickly disappear.





We have, then, in mixtures of water and methyl alcohol, as in mixtures of water and ethyl alcohol, perfectly definite absorption bands of neodymium chloride corresponding to each of the solvents present.

Jones and Anderson conclude, from their work, that the facts which they have brought to light can be explained only in terms of the solvate theory of solution. The different spectra in the different solvents are due to a combination between the solvents and the dissolved substances.

# 12. WORK OF JONES AND STRONG ON THE ABSORPTION SPECTRA OF SOLUTIONS.

Jones and Strong <sup>50</sup> continued the work on the absorption spectra of solutions for three years, and studied in all more than 4000 solutions. They studied neodymium and uranium salts in a great variety of solvents, and found a large number of examples of "solvent bands"—*i.e.*, where a salt dissolved in different solvents had different absorption spectra.

One of the best examples of "solvent" bands is Fig. 8. a is the spectrogram of uranous bromide in a mixture of water and methyl alcohol, and b is the spectrogram of uranous chloride in a mixture of water and methyl alcohol.

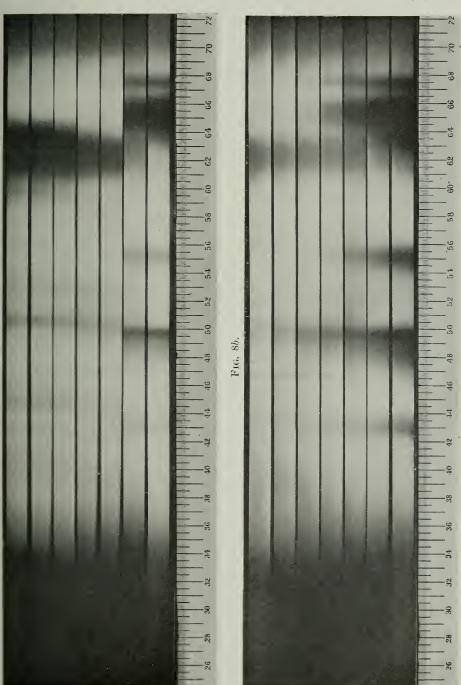
The aqueous solutions are at the bottom of the spectrograms, and as we go up more and more alcohol is added from strip to strip. We see the "water" bands strong at first, rapidly disappear; and the "alcohol" bands at first weak, increase in intensity as the amount of alcohol present relative to the water increases.

We have here two entirely distinct sets of bands, one corresponding to each of the solvents present. A better example than this of solvent bands could hardly be imagined.

Having found such abundant evidence of the effect of the solvent on the power of the dissolved substance to absorb light, in the case of the few solvents referred to above, it seemed very desirable to bring other solvents within the scope of this work, and this has been done. Since the neodymium absorption lines and bands are very sharp, it was selected as the principal substance to be used in this connection. This phase of the work has been carried out recently by Dr. Strong and myself.

<sup>&</sup>lt;sup>50</sup> Carnegie Institution of Washington, Publications Nos. 130 and 160. Amer. Chem. Journ., 43, 37, 97 (1910); 45, 1, 113 (1911); 47, 27, 85 (1912).

F1G. 8a.



#### Uranium Salts.51

An elaborate study was made of the absorption spectra of uranium salts, to see whether any evidence was obtainable for the existence of definite solvate bands in different solvents. We studied both uranyl and uranous compounds.

It was soon found that an aqueous solution of uranyl chloride shows absorption bands in different positions from those of solutions in methyl alcohol. These differences were sufficiently great to merit careful study.

What these differences are can be best seen by giving the wave-lengths of a few bands in the different solvents.

### Uranyl Chloride.

4170,	4315,	4460,	4560,	4740, and 4920
4220,	4345,	4465,	4590,	4760, and 4930
4250,		4400,	4580,	4750, and 4900
4230,		4400,	4580,	4750, and 4910
4250,		4360,	4560,	4750
4240,		4390,	4560,	4750, and 4970
		λλ4400,	4560,	4720, and 4900
4160,		4300,	4444,	and 4630
4160,	4280,	4440,	4620,	4790, and 4920
4140,	4260,	4400,	4540,	4720, and 5050
		λλ4450,	4650,	and 4840
	4220, 4250, 4230, 4250, 4240, 4160,	4220, 4345, 4250, 4230, 4250, 4240, 4160, 4160, 4140, 4280, 4140, 4260,	4220, 4345, 4465, 4250, 4400, 4230, 4400, 4250, 4360, 4240, 4390, \(\lambda\lambda\text{4400}, 4160, 4280, 4440,	4220, 4345, 4465, 4590, 4250, 4400, 4580, 4230, 4400, 4560, 4240, 4560, 4560, 4240, 4560, 4300, 4560, 4160, 4280, 4440, 4620, 4140, 4260, 4400, 4540,

The absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol were photographed. The absorption in pure methyl alcohol was much greater than in pure water. As water was added to the alcoholic solution the absorption became less and less. In the mixed solvents the bands became very broad. A careful study of the structure of these broad bands showed that they were the "water" and "alcohol" bands coexisting; and not one set of bands shifted in position, and this, as we shall see, is an important point.

A simple method of reducing uranyl to uranous salts in solution was found to be the action of nascent hydrogen. This was obtained by introducing into the aqueous solution of the uranyl salt a bar of zinc, and then adding the acid of the salt in question. In this way uranous salts could be prepared, and several of them were found to have sufficient stability for our purpose. Uranous

<sup>&</sup>lt;sup>51</sup> The following pages are taken from a paper which recently appeared in the *Philosophical Magazine*.

chloride, uranous bromide, and uranous acetate were thus made and their absorption spectra photographed and studied. These salts proved to be very useful for the detection of "solvent" bands, or the effect of the solvent on the absorption spectra of salts dissolved in it. The uranous bands are numerous, and, what is far more important for our work, they are well defined, with comparatively sharp edges, and their wave-lengths can be accurately determined. In this respect they are second only to certain lines of neodymium. Some of the most conclusive evidence for solvation in solution, furnished by our spectroscopic work, was with the uranous salts.

The spectrum of uranous chloride in water is quite different from the spectrum in methyl alcohol, and this, in turn, very different from the spectrum in acetone. A glance at the plate for these solutions would lead us to conclude that we were dealing with three very different absorption spectra.

In a mixture of water and methyl alcohol, as the amount of water increases the water band  $\lambda6750$  comes out, gradually increasing in intensity. The methyl alcohol band  $\lambda5050$  to  $\lambda4850$ , which is probably double, narrows on the red side into a band at  $\lambda4850$ . Methyl alcohol bands  $\lambda4770$  and  $\lambda4600$  practically disappear and  $\lambda4670$  becomes very weak. In their places appear the water bands  $\lambda4700$  and  $\lambda4550$ . The methyl alcohol band,  $\lambda4300$  to  $\lambda4450$ , becomes weaker and breaks up into a band at  $\lambda4400$  and a band at  $\lambda4280$ . The methyl alcohol bands  $\lambda4230$  and  $\lambda4120$  apparently come together, as the amount of water present relative to methyl alcohol increases, and becomes the water band at  $\lambda4160$ .

It is thus obvious that the aqueous solution shows very different absorption bands from the solution of uranous chloride in methyl alcohol.

The addition of ethyl alcohol to an aqueous solution of uranous chloride produces a marked change in the spectrum, the ethyl alcohol bands being very different from the water bands. As the amount of ethyl alcohol present relative to water increases, the ethyl alcohol bands come out and the water bands gradually disappear.

The addition of acetone to a methyl alcohol solution of uranous

chloride brings out a number of "acetone" bands between  $\lambda6000$  and  $\lambda6500$ . A strong absorption band also appears from  $\lambda6500$  to  $\lambda6800$ . There is also an acetone band at  $\lambda5600$ .

The addition of acetone to a methyl alcohol solution of uranous chloride produces a marked change in the spectrum, the "acetone" bands being very different from the "water" bands. The acetone solution absorbs much less in the region  $\lambda 6500$ . The aqueous solution has a characteristic band at  $\lambda 6750$ . There are acetone bands at  $\lambda 4920$ ,  $\lambda 4750$ , and  $\lambda 4590$ ; and water bands at  $\lambda 4980$ ,  $\lambda 4700$ , and  $\lambda 4570$ . The absorption of uranous chloride in ethyl alcohol is very similar to the absorption in methyl alcohol, as would be expected; the methyl alcohol bands being of slightly shorter wave-lengths.

The absorption spectrum of uranous chloride in glycerol was photographed, also when water was added to the glycerol solution.

The absorption spectrum in glycerol was found to be very different from what it was in water.

The absorption spectrum of uranous chloride in a mixture of methyl alcohol and ether was photographed. The methyl alcohol solution showed complete ultraviolet absorption to wavelength  $\lambda_{3700}$ . The addition of ether increased the absorption, the absorption of the short wave-lengths extending now to  $\lambda_{3800}$ .

In methyl alcohol there was considerable general absorption in the region  $\lambda_{4300}.$  With the addition of ether the absorption was almost complete from  $\lambda_{4100}$  to  $\lambda_{4450}.$  The addition of ether caused the uranyl bands to shift slightly towards the red without, however, changing their general character. The magnitude of this shift can be seen from the following table.

URANYL CHLORIDE BANDS IN METHYL ALCOHOL. λλ 3880, 4000, 4110, 4240, 4400, 4610, 4780, 4930, 5050, 4135, 4285.

Uranyl Chloride in Methyl Alcohol to which Ether is Added. λλ 3890, 4010, 4140, 4260, 4440, 4630, 4790, 4960, 5050.

The effect of the presence of ether is thus very pronounced, not only causing the bands to shift slightly towards the red, but also increasing the amount of absorption.

It should be stated that in the work with the uranous salts there were present in the solution, in addition to the salt, a little of the free acid of the salt and a small amount of the zinc salt. While these probably had a slight effect on the absorption spectra, the effect must have been far too small to have produced such changes as those recorded above for the different solvents.

Having found such abundant evidence for the effect of the solvent on the power of the dissolved substance to absorb light, in the case of the few solvents referred to above, it seemed very desirable to bring other solvents within the scope of this work, and this has been done. Since the neodymium lines and bands are very sharp, it was selected as the principal substance to be used in studying the effect of the solvent on the absorption spectra of the dissolved substance, where a large number of solvents was to be employed. This phase of the work has been very recently carried out by Jones and Strong.

#### Absorption Spectra of Neodymium Salts.

The following nomenclature will be used in describing the neodymium absorption spectra:

 $\alpha$  group in the region  $\gamma$ 3400 to  $\gamma$ 3600.

at about  $\gamma$  4300.

" from  $\gamma 4600$  to  $\gamma 4800$ .
" from  $\gamma 5000$  to  $\gamma 5400$ .
" in the region  $\gamma 5800$ .

at  $\gamma$ 6300.

In designating the neodymium spectra we start from the violet end of the spectrum. This is the natural method when a grating is used. It is doubtful whether, in the near future, the ultraviolet spectrum of neodymium can be studied much farther than we have done, so that this is the natural end of the spectrum at which to begin. It is, on the other hand, probable that there are many neodymium bands farther down in the infrared than we have gone; and when these have been worked out they can then be named in the natural order.

The change in the absorption spectrum of neodymium chloride as the solvent is changed can be seen best by expressing the results in the following form. The abbreviations used are "d." diffuse. "fa." faint, "fi." fine, "h." hazy, "i." intense, "n." narrow, "sh." sharp, "st." strong, "we." weak, "wi." wide.

The following results obtained with neodymium chloride show the effect of the solvent on the absorption spectra of solutions of this compound. The bands of the different solvents have different wave-lengths and different relative intensities.

Having found that the solvent played an important part in determining the absorption of light by the dissolved substances, Jones and Strong used *isomeric organic solvents* to see whether such closely related compounds would affect differently the power of substances dissolved in them to absorb light. They prepared solutions of neodymium chloride in propyl and isopropyl alcohols, and in butyl and isobutyl alcohols, and photographed the absorption spectra of this salt in these isomeric solvents. The following results show different absorption lines and bands in the isomeric solvents:

			a GROUP.			
In water.	In methyl and ethyl alcohols.	In propyl al- cohol.	In isopropyl alcohol.	In butyl al- cohol.	In isobutyl alcohol.	In glycerol.
λλ 3390 we. 3465 n. st. 3505 n. st. 3540 n. st. 3560	λλ 3475 fa. 3505 3560 wi. i.	λλ 3545 sh. 3460 3490 3510 we. 3525 st. 3540 st. n. 3560 d. 3580 we.	λλ 3460 3510 3535	λλ 3450 sh. n. 3460 we. 3492 d. 3535 sh. n. 3545 3560 d.	λλ 3455 we. 3485 st. 3515 we. 3545 3570	3475 st.
		-	8 GROUP.			
In water.	In methyl and ethyl alcohols.	In propyl al- cohol.	In isopropyl alcohol.	In butyl al- cohol.	In isobutyl alcohol.	In glycerol.
λλ 4271 sh. 4290 n. we.	λλ 4290 4325	λλ 4270 we. 4285 4330 wi. we 4450 wi. we	λλ 4265	λλ 4265 4285 4300	λλ 4300 we.	λλ 4288 sh. 4270 fi. 4305 fi.
			γ GROUP.			
In water.	In methyl and ethyl alcohols.	In propyl al- cohol.	In isopropyl alcohol.	In butyl al- cohol.	In isobutyl alcohol.	In glycerol.
λλ 4610 h. 4645 we. 4685 4755 sh. 4820 ni.	λλ 4700 4780 4825	λλ 4600 we. d. 4700 4770 4830	λλ 4600 d. 4690 4730		λλ 4700 4730 4780 4830 4880 we.	λλ 4620 4710 4730 4760 4790 4840

δ GROUP.

In water.	In methyl and ethyl alcohols.	In propyl al- cohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 5090 n. 5125 wi. h. 5205 i. n. 5222 i. n. 5255 n. 5315 fa. h.	λλ 5125 h 5180 h. fa. 5220 i. n. 5245 i. 5290 n. 5315 fa.	λλ 5130 wi. d. 5180 wi. d. 5220 5230 5250 5290 5330 we.	λλ 5100 wi. d. 5320 wi. d.		λλ 5150 5260 5215 5230 5250 5300	λλ5120 wi.h. 5170 n. 5190 n. 5230 5240 5250 5270 we.
	·		e Group.			
In water.	In methyl and ethyl alcohols.	In propyl al- cohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 5725 n. st. 5745 st. 5765 st. 5795	λλ 5725 h. 5765 n. 5800 st. 5835 i. 5860 h. 5895 fa. 5925 fa.	λλ 5740 5780 5810 5850	λλ 5720 d. 5780 5810	λλ 5750 5780 5820 5860 5900 5930	λλ 5740 we. 5810 st. 5850 st. 5890 5920 5950 we. 5995 we. 6020 we.	5790 5805 5820 5850

If we compare carefully the spectra of neodymium chloride in butyl and isobutyl alcohols, we find that the bands are weak and diffuse in isobutyl alcohol, and have different relative intensities from what they have in the butyl alcohol. The bands in butyl alcohol are very much finer and sharper than they are in isobutyl alcohol. Further, the bands of neodymium chloride in isobutyl alcohol have slightly greater wave-lengths than in butyl alcohol.

To eliminate the possibility of the effect of the solvent on absorption spectra being due to anything inherent in the nature of neodymium chloride, the nitrate of neodymium was studied in the same way as the chloride.

The absorption spectra of neodymium nitrate in water, in methyl alcohol, in ethyl alcohol, in mixtures of these alcohols and water, in propyl and isopropyl alcohols, in butyl and isobutyl alcohols, in acetone and in mixtures of acetone and water, in ethyl ester and in formamide, were carefully photographed and studied. Results will be given in the case of neodymium nitrate only for the  $\alpha$  bands.

#### a Bands.

*In water.* Practically the same as the bands of neodymium chloride, but the bands of the nitrate are broader and hazier than those of the chloride.

Vol. CLXXVI, No. 1055—38

In methyl and ethyl alcohols. There are only two bands in the  $\alpha$  group,  $\lambda_{3465}$  and  $\lambda_{3545}$ .

In propyl alcohol.  $\lambda\lambda_{3455}$ , 3500, and 3585.

In isopropyl alcohol.  $\lambda\lambda_{3460}$ , 3505, and 3535.

In butyl alcohol.  $\lambda\lambda_{3450}$ , 3500, and 3540.

In isobutyl alcohol. Ultraviolet absorption was so great that on the plate taken the a group did not appear. The absorption in general is the same as that of the chloride in this alcohol.

In acetone.  $\lambda\lambda_{3475}$  and 3555.

In ethyl ester.  $\lambda\lambda_{3455}$ , 3500, and 3540.

The other groups of absorption bands of neodymium nitrate in the different solvents show differences in the wave-lengths comparable with the above; but these results suffice to show the effect of the solvent on the power of neodymium nitrate to absorb light.

The above evidence that the solvent plays an important part in the absorption of light by substances dissolved in it is strong. When we take into account the number of salts studied and the number of solvents employed, the evidence is little short of proof. The only reasonable question is, How are we to interpret these facts? Before attempting to answer this question we should take into account also the following fact. A salt dissolved in a given solvent is characterized by a definite absorption spectrum. When a salt is dissolved in mixtures of varying proportions of two solvents only two definite absorption spectra appear, one being characteristic of each solvent. One spectrum does not gradually change into the other as the composition of the mixed solvent changes, but only the relative intensities of the two spectra vary. Starting with that mixture of the two solvents in which both of the spectra are equally intense, if we diminish the amount of a relative to b, the spectrum corresponding to a becomes feebler and feebler, and the spectrum corresponding to b more and more intense. This fact was first noted by Jones and Anderson, and since repeatedly confirmed by the work of Jones and Strong. We found that when neodymium chloride was dissolved in a mixture of methyl alcohol and water, it showed a definite set of "water" bands and a definite set of "methyl alcohol" bands. As the amount of water in the solution was

decreased relative to the alcohol, the "water" bands decreased in intensity but remained in the same position. As the amount of alcohol in the solution was decreased relative to the water the "alcohol" bands decreased in intensity, but their position remained unchanged.

Jones and Anderson interpreted these facts as strong evidence in favor of the view that there are definite hydrates and definite alcoholates in the solution.

The spectroscopic evidence for solvation in solution furnished by Jones and Anderson has, as has already been stated, been increased many fold by the work of Jones and Strong. A large number of solvents and a fairly large number of salts have been used, and the existence of solvent bands in general established.

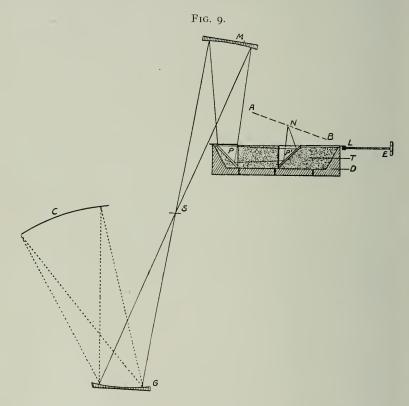
The question of the relative stability of the different solvates with respect to various physical and chemical agents, has been studied at length by Jones and Strong by means of absorption lines and bands. It would lead us beyond the scope of this paper to discuss these results in detail. Suffice it to say that the hydrates in general are the most persistent of all the solvates, although this depends upon the conditions to which the solution is subjected.

Taking all of the spectroscopic work into account, I regard the evidence from this source as strongly supporting the solvate theory of solution as advanced in this laboratory more than a dozen years ago.

Jones and Strong studied the effect of rise in temperature on absorption spectra, both over the range 0° to 100° in open apparatus, and in closed apparatus up to much higher temperatures. The open apparatus is shown in Fig. 9. N is a Nernst glower, arranged to slide along the rod AB. P and P' are quartz prisms which are held by a lid L. The prism P is stationary, whereas the prism P' can be moved by the travelling carriage E back and forth through the trough T, which contains the solution whose absorption spectra is being investigated. AB is so inclined that the optical length of the light beam from N to P'P and the concave mirror M shall be constant, whatever the length of the solution between P and P' may be. The greatest length of path PP' used was 200 mm. The hypothenuse faces of P and P' are backed by air films which are enclosed by glass plates cemented to the quartz prisms.

Considerable difficulty was experienced in finding a cement

that would adhere to the polished quartz prisms at the higher temperatures. For aqueous solutions baked caoutchouc was found to work very well. D is a brass box holding the trough T. D is filled with oil and placed in a water-bath whose temperature can be varied between  $0^{\circ}$  and  $90^{\circ}$ . The path of the beam of light is then from the Nernst glower N, or spark, to the quartz

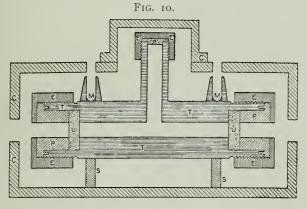


prism P'. The light is totally reflected from the hypothenuse face of this prism through the solution to P. This prism also has its hypothenuse face backed by an air-film, so that the light is totally reflected upward to the concave speculum mirror at M.  $M_1$  focuses the light on the slit of the Rowland concave grating spectroscope, G being the grating and  $C_1$  the focal curve of the spectrum. This prism arrangement was designed by Dr. Anderson. It was found to work very well.

From the study of the effect of temperature on absorption spectra over the range o° to 90° Jones and Strong concluded that "rise in temperature causes the general absorption of any salt in water to increase, and also causes the bands to broaden and become more intense."

The closed apparatus used by Jones and Strong is shown in Fig. 10.

Two cells, one 1.0 cm. and the other 10 cm. in length, were used. Fig. 10 represents a longitudinal section of the longer cell. Since both cells were exactly alike in all respects except in length and in the size of the side tube, only the longer cell is described here.



The main part of the cell (I) was made of tool steel, and was heavily copper plated and gold plated on all the inner surfaces. The side tube was very tightly fitted into the main part of the horizontal tube. The open part of the tube was 1.0 cm. in diameter. The windows of the cell (U,U) were 2.5 cm. in diameter and were either of quartz or glass. One of the troubles with this form of cell is the formation of precipitates on the inside surfaces of the windows. Every time a precipitate is formed the windows have to be taken out and cleaned. On being put back there is always great danger of the quartz or glass ends being broken. During the work a number of ends were broken in this way.

Quartz ends are much tougher and less easily broken than glass ends. They are, however, quite expensive, and in most of the work the solutions were not transparent in the ultraviolet. For this work glass ends were used. Some of these were cut out of ordinary plate glass, and others were made from "uviole" glass, which is tougher and much more transparent in the ultraviolet than is the ordinary plate glass. For cutting the ends a steel tube 2.5 cm, in diameter was fastened to the axle of an ordinary fan motor in such a way that the tube was vertical, the free end of the steel tube being at the bottom. An old glass end was then cemented to a piece of plate glass with hot sealing wax and served as a guide for the steel tube. The plate glass was then held against the end of the steel tube and the motor started. Wet carborundum was fed constantly against the grinding steel tubes. Plates nearly 1.0 cm. thick could be cut in this way in 20 or 30 minutes.

The quartz windows rested on gold washers which, in turn, rested directly against the gold-plated shoulders of the tube T. P P P are plungers. Two of these at the ends of the main tube have guide pins that prevent them from turning. Between the plungers and the windows were placed washers. Various kinds of washers of hard leather, lead, zinc, etc., were used. The leather washers, however, seemed to be the most satisfactory. Steel caps, E E E, serve to tighten the plungers. M M are receptacles for thermometers. C is an iron air-bath and prevents rapid changes in temperature in the cells.

In heating a cell of this kind it was found that the rise in temperature must be very gradual. Very great difficulty was encountered in getting the ends to hold liquid-tight. The screw ends were tightened gradually for several days and for several heatings. On one occasion, when the tube was filled with one of the higher alcohols, a very effective closing was made. is possible that dried films of oils (like linseed oil) might be of use as washers.

This cell worked well in nonaqueous solutions, but water rusted it at the higher temperatures. Another form of cell, to be described later, was used with aqueous solutions at the higher temperatures.

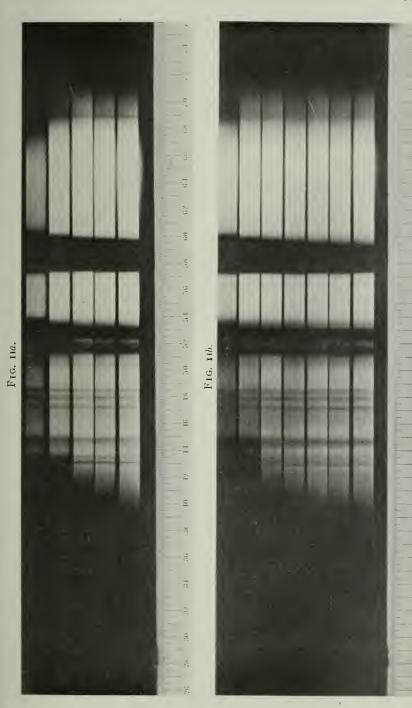
The following spectrogram will show the general character of the results obtained in nonaqueous solvents:

Neodymium Chloride in Methyl Alcohol.—Fig. 11 represents the absorption of a 0.1 normal solution of neodymium chloride

-5

-8

<u>×</u>



in methyl alcohol, 10 cm. in length. This spectrogram shows the methyl alcohol bands quite sharply. A weak band appears on the first strip  $\lambda$ 4015, and at  $\lambda$ 4200. The band  $\lambda$ 4285 is quite strong and only about 10 Angström units wide. A weak and quite narrow band appears at  $\lambda 4270$ . The band  $\lambda 4270$  is rather hazy; \(\lambda\_{4450}\) is about 50 Angström units in width and is very diffuse, its red side not being as diffuse as the violet side. The band  $\lambda_4620$  is very weak,  $\lambda_{4700}$ ,  $\lambda_{4770}$ , and  $\lambda_{4820}$  all have about the same intensity and width; the first two being accompanied by very weak bands on their violet sides at \$\int\_{4680}\$ and  $\lambda_{4750}$ . The band  $\lambda_{5040}$  is very weak and broad;  $\lambda_{5120}$  is about 20 Angström units wide and is very strong. The band  $\lambda_{5175}$  is very similar to  $\lambda_{5120}$ , except that it is only about onehalf as intense. The bands  $\lambda_{5215}$ ,  $\lambda_{5250}$ , and  $\lambda_{5290}$  are all very intense and are quite sharp, the middle band being about 20 Angström units in width, while the other two are only about 10 Angström units wide. There is a wide absorption band from  $\lambda$ 5710 to  $\lambda$ 5040, with the sharper edge on the violet side. The red band at  $\lambda6850$  appears to be quite strong and about 20 Angström units in width.

The other strips represent the same solution at different temperatures, these being 15°, 26°, 40°, 55°, and 78°, starting with the lowest strip.

With rise in temperature the bands all become somewhat more intense and wider. The general absorption over the whole spectrum region increases, especially at the higher temperatures, and begins to encroach quite rapidly on the violet and red regions. This violet absorption is probably a general absorption, but the encroaching on the red side is probably due to the increase in the intensity of the group of red bands.

In the upper strip transmission extends from about  $\lambda 4200$  to  $\lambda 6100$ . A very weak band appears at  $\lambda 4200$  and another one at  $\lambda 4305$ . The bands in the blue and green have changed but little. Absorption is pretty complete from  $\lambda 5100$  to  $\lambda 5190$ ,  $\lambda 5210$  to  $\lambda 5350$ , and  $\lambda 5690$  to  $\lambda 5990$ . Weak bands appear at  $\lambda 6230$ ,  $\lambda 6280$ , and  $\lambda 6750$ . If any of the bands showed any shift it was too small to measure. The band at  $15^{\circ}$ , extending from  $\lambda 5710$  to  $\lambda 5940$ , widens approximately 20 units on its violet side and 50 units on its red side. It is probably more or less general that wide

absorption bands usually broaden unsymmetrically towards the red, especially when this side is the more diffuse.

A spectrogram representing the absorption of a methyl alcohol solution, 0.2 normal and 1.0 cm. in length, was made. The temperatures were  $25^{\circ}$ ,  $40^{\circ}$ ,  $55^{\circ}$ , and  $70^{\circ}$ . The only important change due to temperature was at  $70^{\circ}$ , the intense absorption near the centre of the  $\epsilon$  group of bands having practically disappeared.

Neodymium Bromide in Methyl Alcohol.—B, Fig. 11, represents the absorption spectrum of a 0.1 normal solution of neodymium bromide in methyl alcohol. The length of cell was 10 cm. The temperatures were 25°, 35°, 44°, 60°, 82°, 100°, and 120°, beginning with the lowest strip. At the highest temperature a slight precipitate was formed, but still some light was transmitted. The neodymium solutions all become much more deeply colored at the higher temperatures, as can easily be shown by heating such a solution in an ordinary test-tube.

The absorption spectrum of neodymium bromide in methyl alcohol is quite different, so far as minute detail goes, from that of the chloride. In general, the bands of the chloride are from 5 to 15 Angström units farther towards the red than the bromide bands.

For the lowest strip, very weak and diffuse bands appear at about  $\lambda_{4000}$ ,  $\lambda_{4180}$ ,  $\lambda_{4600}$ ,  $\lambda_{4900}$ ,  $\lambda_{5040}$ ,  $\lambda_{5320}$ ,  $\lambda_{6230}$ ,  $\lambda_{6260}$ ,  $\lambda_{6730}$ , and  $\lambda_{6790}$ . The  $\beta$  group of the bromide is very different from that of the chloride. It consists of a very sharp, narrow (3 units) band at  $\lambda_{4625}$ , a very sharp and less intense band at  $\lambda_{4275}$ , a hazy band at about  $\lambda_{4280}$  which more or less overlaps  $\lambda_{4275}$ , and at higher temperatures  $\lambda_{4275}$  cannot be noticed at all. A very weak band appears at  $\lambda_{4300}$ , and a broader band, about 20 Angström units in width, at  $\lambda_{4325}$ .

The  $\gamma$  group of the chloride is also quite different from that of the bromide, which has four bands of almost equal intensity at  $\lambda_{4690}$ ,  $\lambda_{4745}$ ,  $\lambda_{4765}$ , and  $\lambda_{4815}$ . Weak bands appear at  $\lambda_{4670}$ ,  $\lambda_{4700}$ , and  $\lambda_{4725}$ . The  $\delta$  group consists of a rather narrow band at  $\lambda_{5090}$  and a very strong band at about  $\lambda_{5115}$ ; a lot of narrow and intense bands at  $\lambda_{5200}$ ,  $\lambda_{5220}$ ,  $\lambda_{5235}$ ,  $\lambda_{5250}$ , and  $\lambda_{5275}$  practically merge into a single band. The  $\varepsilon$  group consists of a single wide band extending from  $\lambda_{5700}$  to  $\lambda_{5880}$ .

As the temperature is raised the violet increases quite rapidly, and the  $\delta$  and  $\epsilon$  groups of bands become wider and stronger. The later band widens very greatly towards the red. All the bands become very much more diffuse. This is particularly true of the  $\beta$  group, since at 120° only two very hazy, indistinct bands appear; while at 25° some of the bands in this group were almost as fine as spark lines.

No measurable shift of the bands towards the red could be observed.

That the absorption spectra of the chloride and the bromide in methyl alcohol would be so different was quite unexpected, since these two salts have almost identically the same absorption spectra in aqueous solution.

#### DISCUSSION OF RESULTS OBTAINED BY JONES AND STRONG.

(1) The general effect of rise in temperature is to give a solution of an inorganic salt a deeper color. This deepening of the color signifies that the absorption of light has become more selective, and spectroscopic work indicates that this selective absorption is usually due to a widening of the absorption bands. As these bands are never so distributed over the spectrum as to give a colorless solution, it follows that a widening of the absorption bands will intensify the color of the solution. In many cases this widening appears to be quite unsymmetrical, but this need not necessarily mean that the centre of gravity of the individual absorption band is shifted. Many examples of the neodymium absorption bands show this phenomenon very clearly. For instance, the absorption due to the  $\gamma$  and  $\delta$  groups of bands may be sufficiently intense to make these groups appear as single bands. If the absorption is not so intense as this, in some solvents it is found that with rise in temperature the shortest wave-length bands may decrease in intensity, and may even disappear. The long wave-length bands increase in intensity, and in some cases new bands appear. Knowing this, it is easy to understand that if the absorption is so strong that each of these groups of bands appears as a single band, these broad bands will widen very unsymmetrically towards the red with rise in temperature. It may be that some change like this takes place in the case of the uranyl bands. It is for this reason that a formula calculated for the widening of a band with rise in temperature would not apply to many wide bands.

- (2) In the case of all pure salts dissolved in a single solvent the bands have been found to widen with rise in temperature, and at the same time they become more diffuse, the edges becoming hazier. When there is a mixture of salts in the same solvent, the bands may become much weaker with rise in temperature. This is the case in a mixture of neodymium and calcium chlorides in water. In a similar manner, the absorption of a salt in two solvents probably decreases in intensity with rise in temperature. An example of this kind is that of uranous bromide in 40 per cent. water and 60 per cent. alcohol. At ordinary temperatures the bands are of about equal intensity. At 80° the water bands have practically disappeared, without the alcohol bands having widened to any great extent.
- (3) In general, the centre of intensity of single bands changes but little. Whenever there is any change of wave-length, the shift is invariably towards the red. It seems that this shift is greater the wider the band, so that it is difficult to say in most cases whether the shift is real or only apparent. In the case of solutions of pure neodymium and erbium salts the shift is, in general, too small to be observed.
- (4) A study of gaseous aggregates, such as  $N_2O_4 \longrightarrow 2 NO_2$ , indicates that raising the temperature or lowering the pressure increases the relative number of the simpler molecules. Many vapors like those of the fatty acids show molecular clustering at low temperatures. In a similar manner, it would be expected that aggregates would gradually break down at the higher temperatures. In considering specific examples it would be expected that the breaking down of acid uranyl sulphate aggregates would result in a shift of the uranyl bands, the shift being towards the violet. On the other hand, if the nitric acid uranyl nitrate aggregates are broken down, it would be expected that the uranyl bands would be shifted towards the red. Acording to this view, the shift of the uranyl bands of uranyl nitrate in nitric acid and of uranyl sulphate in sulphuric acid, with rise in temperature, should be quite different if the only effect of rise in temperature is a breaking up of the aggregates.

In advancing a hypothesis of this kind it is assumed that it is only the molecules in an aggregate that are effective in changing the frequency of vibration of the absorbing systems of the light centres. This means that the kinetic energy of the aggregate corresponds to that of a molecule at the same temperature in the solution, the individual molecules in an aggregate all moving together. Whether there is a constant interchange of these molecules and the molecules of the solution, spectroscopic evidence does not as yet show. Neither can it be said with certainty that molecules outside the aggregates do not affect the frequencies of vibration of the absorbing system within the aggregate. Assuming that this is not the case, then it follows of necessity that with rise in temperature the acid aggregates are not broken up, because the uranyl bands of acid solutions are then shifted to the red. This shift seems to be about as great for uranyl sulphate in sulphuric acid as it is for uranyl nitrate in nitric acid. In a similar manner, acid solutions of neodymium salts do not have their absorption spectra changed with rise in temperature so as to resemble more closely that of the neutral salt, as one would expect if the acid neodymium aggregates were broken down.

- (5) When foreign salts like calcium chloride are added to solutions of neodymium chloride, it is probable that aggregates containing the two salts are formed. In the case of aqueous solutions of these salts, it is found that the neodymium bands are shifted to the red with rise in temperature, whereas aqueous solutions of pure neodymium chloride do not show this effect at all. Exactly what takes place in this case is not evident.
- (6) The effect of rise in temperature on solutions showing the solvate bands of equal intensity, has been to cause a change in the intensity of the solvate bands; very little, if any, change, however, in the wave-lengths of the bands takes place. In the case of water and alcohol, the alcohol bands increase in persistency as the temperature is raised.
- (7) In the work with the closed cell at high temperatures, it was found that precipitates were formed in practically every case, probably due to hydrolysis, alcoholysis, etc.; precipitation taking place in dilute as well as in concentrated solutions. Several examples were tested of concentrated solutions of colored salts mixed with calcium or aluminium chloride, and precipitation was found to take place under these conditions at comparatively low temperatures. It would be very interesting to learn whether acid

aggregates of uranyl, neodymium, erbium and such salts are less likely to form precipitates than the neutral salt solutions.

In the case of neutral uranous solutions these precipitates form at 70° or 80°. The presence of acid prevents this precipitation at temperatures below 100°.

Whether the salt precipitation at high temperatures is complete or not cannot be decided in general at present. In the case of several neodymium and erbium solutions this seemed to be the case. In one of the uranyl solutions, however, some uranyl salt remained in the solution after the precipitate had settled.

- (8) It may be said, in general, that there is a very great increase in the absorption of all solutions in the short wave-length region of the spectrum as the temperature is raised. How great this increase in absorption would be if pure solutions were used has not yet been determined. The formation of precipitates is usually preceded by a very great increase in the short wave-length absorption.
- (9) The problem as to whether a rise in temperature produces a permanent change in the structure of the aggregates in solution has not been studied to any great extent. In the case of the existence of two solvent spectra it is found that the spectra, on cooling the solution, are exactly the same as before heating. In the case of an acetone solution of uranyl chloride it was found that the bands are apparently single after the precipitate was formed during the heating. Whether these bands would have become double again when the solution was cooled was not tested. It would be interesting to learn whether selective solvate precipitation would take place on heating solutions.

### Absorption Spectra and the Solvate Theory of Solution.

The first direct spectroscopic evidence for the existence of solvates was furnished by Jones and Anderson in their study of salts of neodymium. A salt like neodymium chloride was found to have a very different absorption spectrum in water from what it had in methyl alcohol. Neodymium chloride in the proper mixture of water and methyl alcohol shows both the "water" bands and the "alcohol" bands. By varying the amounts of the solvents relative to one another the relative intensities of the two sets of bands can be changed at will.

Neodymium nitrate in a mixture of water and the alcohol, shows bands of the same character in the two solvents as the chloride.

Praseodymium chloride in a mixture of water and methyl alcohol shows the same kind of change as neodymium chloride. In this case an entirely new band appears in the alcohol, which has no analogue in the aqueous solution.

The existence of "water" bands and "alcohol" bands in the aqueous and alcoholic solutions, respectively, was interpreted by Jones and Anderson as direct evidence for the existence of hydrates in the aqueous solutions and of alcoholates in the alcohol solutions—in a word, is direct spectroscopic evidence for the solvate theory.

The largest amount of, and most direct spectroscopic evidence for the solvate theory of solution has been brought to light by our work, which has been in progress continuously during the past three years. A careful study was made of the absorption spectra of cobalt salts in different solvents and as affected by temperature. Glycerol solutions of these salts showed a different spectrum from aqueous solutions, indicating the presence of glycerolates in such solutions, as we have hydrates in aqueous solutions.

The effect of rise in temperature is to increase enormously the absorption of concentrated aqueous solutions of cobalt chloride, especially in the red. It is well known that such solutions turn blue on heating. The more concentrated the solution the lower the temperature at which this color change takes place. There is a large amount of evidence which points to the conclusion that this change in absorption is due to a breaking down of the more complex hydrates with rise in temperature. If this is the true explanation of the phenomenon, the presence of a dehydrating agent such as calcium chloride or aluminium chloride ought to cause this change in absorption to take place at a lower temperature, since the dehydrating agent would assist the rise in temperature in breaking down the complex hydrates.

The results here are in accord with prediction. The addition of either of the above chlorides causes the great absorption in the red to take place in more dilute solutions at the same temperature, or in a given solution at a lower temperature.

It was further found that the temperature at which this marked change in the red absorption takes place is higher for aqueous and glycerol solutions than for solutions in other solvents, showing that the "hydrates" and "glycerolates" are more stable with respect to temperature than other solvates.

The effect of rise in temperature on salts of chromium was also studied, and was shown to be similar to the effect of rise in temperature on cobalt salts—the higher the temperature the greater the absorption.

#### WORK OF JONES AND GUY.

Jones and Guy studied the effect of high temperature on the absorption spectra of solutions, using the following form of apparatus devised by Strong.

The reason that the work of Jones and Strong was not pushed to higher temperatures, with aqueous solutions, was that the form of apparatus then in use did not admit of it. This consisted of a steel tube, <sup>52</sup> lined on the inside with copper and plated with gold on all of the inner surfaces. This worked very satisfactorily with nonaqueous solutions, the gold plate adhering firmly to the copper, which, in turn, remained adherent to the steel.

When an aqueous solution was heated in the apparatus from 100° to 200° the result was unsatisfactory. The water, under the high pressure, forced its way through the copper and the gold and rusted the iron, as has already been stated. The result was that the copper with the gold, separated from the steel, and the solutions, after heating for a time, gave the iron reaction. This apparatus had the further disadvantage that when a precipitate formed with rising temperature it was necessary to open the entire apparatus and remove the glass ends in order to clean them.

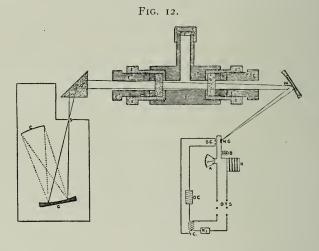
To overcome these difficulties the following form of apparatus (Fig. 12) was constructed by Strong, and used to study the effect of rising temperature on the absorption spectra of aqueous solutions.

The quartz ends are fastened into the ends E'. The plunger P has guide grooves instead of guide pins. A part of the plunger is provided with screw threads for removing it. The entire cap is removed from tube T by unscrewing E', during which the quartz end is untouched. When the ends are removed the quartz window can be easily cleaned. Gold washers were inserted between T and E' and between E' and U.

The general arrangement of the apparatus is also shown in

<sup>&</sup>lt;sup>52</sup> Amer. Chem. Journ., 47, 30 (1912).

Fig. 12. The cell is kept in a horizontal position so that any bubbles that may form will rise in the side tube. The spectroscope, containing the grating G, photographic plate holder C, and slit S, being kept vertically, a  $45^{\circ}$  quartz prism was used to change the horizontal beam of light into a vertical beam; the beam being totally reflected by the hypothenuse surface of O. The source of light N G (Nernst glower) or S G (spark gap) was focused by the concave speculum mirror M on the slit S. A similar arrangement was used for the fused silica cell. D T S is a double-

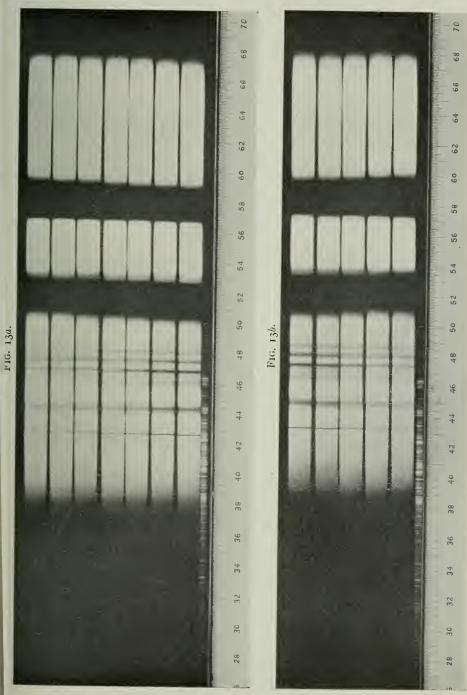


throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. B is a ballast. R is a variable resistance, by means of which the current in the Nernst glower, as shown by the ammeter A, may be kept constant. O C is an oil condenser. I C is an X-ray induction coil, and  $R_2$  is a resistance in the primary circuit of this coil.

One spectrogram will give an idea of the general character of the results obtained.

### Neodymium Chloride in Water (see Fig. 13).

The solution whose spectrum is given in Section A was saturated, the depth of absorbing layer being 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were  $20^{\circ}$ ,  $45^{\circ}$ ,  $70^{\circ}$ ,  $95^{\circ}$ ,  $115^{\circ}$ ,  $140^{\circ}$ , and  $165^{\circ}$ , respectively.



Vol. CLXXVI, No. 1055-39

Absorption bands which are unchanged by the range of temperature from 20° to 200° appear at  $\lambda_3800$ ,  $\lambda_{4025}$ ,  $\lambda_{4200}$ ,  $\lambda_{4325}$ ,  $\lambda_{4440}$ ,  $\lambda_{4600}$ ,  $\lambda_{4690}$ ,  $\lambda_{4750}$ , and  $\lambda_{4820}$ .

The double band from  $\lambda_{5050}$  to  $\lambda_{5270}$  is only slightly affected, if at all.

The two most interesting absorption bands are those whose centres are near  $\lambda_{4275}$  and  $\lambda_{5800}$ . The former of these in strip 1 is very sharp and intense, though only a few Angström units wide. Both edges were well defined. As the temperature is raised the violet edge remains very sharp, while a rapid shading off of the red edge takes place. At a glance the band appears to be less intense in the higher temperature strips, but on close examination it is seen to be more diffuse; the red edge diffusing over a range of about 20 Angström units at the highest temperature. This is exactly in accord with what Jones and Anderson 53 had found. They showed that when the number of molecules in the path of the light was kept constant, this band remained practically constant; while it had been shown by Jones and Anderson and by ourselves, that this band changes with dilution, being more intense in the most concentrated solution.

The  $\lambda_5800$  band is affected most by temperature as well as by dilution. In strip 1 this band is about 200 Angström units wide, and increases regularly in width as the temperature is raised, until at the highest temperature the width is over 250 Angström units; or there is a total widening of 50 Angström units. The violet edge remains perfectly sharp, while the shading is towards the red end of the spectrum.

It occurred to us that whatever effect might be produced by rise in temperature, if it was a true temperature effect the reverse should happen when the solution was allowed to cool.

With this in view B was made. The concentration of the solution and the depth of layer photographed in Section B were exactly the same as in A. In fact, the identical solution was used. As soon as the film A had been exposed with rising temperature, it was removed from the camera and developed. Without even allowing the cell to cool, another film was placed in the camera and Section B made with falling temperature. In B the temperatures were 165°, 140°, 115°, 95°, and 70°, the highest temperature being nearest the numbered scale.

<sup>&</sup>lt;sup>53</sup> Carnegie Institution of Washington, Publication 110.

A study of the original film shows changes only in bands  $\lambda_{4275}$  and  $\lambda_{5800}$ ; and this change is exactly the reverse of that shown by these same bands in A. The  $\lambda_{4275}$  band appears in strip I with a sharp violet edge, and shading off towards the red over a range of 15 or 20 Angström units. As we pass to the succeeding strips in the direction of falling temperature, the red edge becomes sharper and sharper until, in strip 5, which represents the lowest temperature, the band assumes its normal sharp edge on the red side and covers less than ten Angström units. The  $\lambda_{5800}$  band narrows uniformly from the red end, as the temperature falls, the total narrowing being about 40 Angström units.

## THE EFFECT OF DILUTION ON THE ABSORPTION OF LIGHT BY SOLUTIONS.

The question as to the effect of dilution on the power of solutions to absorb light is an old one. This question became especially prominent at the time the theory of electrolytic dissociation was proposed. In dilute solutions of electrolytes there are practically only ions present, very few molecules existing as such. All of the properties of such solutions are the properties of the ions contained in them. Therefore, the power of these solutions to absorb light must be due to the ions present in them. This was the reasoning in vogue, and the conclusion drawn.

It was at the same time freely recognized that molecules in solution have the power to absorb light. This was shown by the fact that solutions of non-electrolytes, or completely unionized substances, are often colored; and color in solution means selective absorption of light.

The result of the conclusion drawn from the theory of electrolytic dissociation, was that an enormous amount of work was done on the absorption spectra of dilute solutions of both electrolytes and non-electrolytes. Ostwald carried out an elaborate investigation on the relation between color and dissociation, and published the work under the title "Ueber die Farbe der Ionen." <sup>54</sup> A large number of salts were brought within the scope of this investigation. Salts of an acid having a colored anion, with colorless cations were studied. This is illustrated by the various permanganates, hydrogen, sodium, ammonium, magnesium, zinc, cad-

<sup>54</sup> Zeit physik. Chem., 9, 579 (1892).

mium, etc. Ostwald showed that these salts of any given acid had essentially the same spectra. In a similar manner, he studied salts of fluorescein, eosin, iodoeosin, resolic acid, diazoresorcinol, etc. Ostwald then reversed the process and compared the salts of a given colored base with colorless acids. Thus, he studied the salts of *p*-rosaniline with acetic, chloric, benzoic, hydrochloric, nitric, butyric, salicylic, lactic, etc., acids, and found practically the same absorption spectra for all of these salts.

From the standpoint from which he undertook his investigation, Ostwald may be said to have solved the problem of the rôle of ions in the absorption of light, so far as that could be done with the prism spectroscope.

The problem that we studied was of a different nature. It had to do with the absorption spectra of ions relative to that of the molecules from which they were formed. Some earlier work of Jones and Anderson <sup>55</sup> had shown that if molecules have different action on light from ions, the difference is slight; indeed, so slight that there would be no hope of detecting it by ordinary means, even with a grating spectroscope. This problem was attacked in the following manner:

### Making a Dilution Spectrogram.

Before entering upon a detailed discussion of the spectrograms it is wise to state briefly the method used in making any given spectrogram. Throughout all the work done on the effect of high dilution on absorption spectra, under the conditions of Beer's law, only three exposures were made for any given spectrogram, —i.e., only three dilutions were compared. The depths of cell in all cases were 0.5 cm., 50 cm., and 250 cm., the dilution being increased one hundred times between the first two solutions and five times between the last two; or a total dilution of five hundred times between the first and last solution. Smaller depths of cell than 5 mm. were not used, on account of the large percentage error in measuring such depths.

Much difficulty was experienced in getting sufficient light through the longer cells to fill the grating completely, nor was this possible unless the tube containing the solution was constantly

<sup>55</sup> Carnegie Institution of Washington, Publication 110.

moved backward and forward so that the image of the source of light was moved along the slit of the camera.

By such a procedure the surface of the grating could be illuminated fairly uniformly, and the exposures gave good results on the photographic plate, as is shown by the spectrograms.

In order to insure complete illumination of the grating a uniform procedure was adopted. The longest cell, containing the most dilute solution, was first placed in position; the light passed through, and the image of the Nernst glower sharply focused on the slit of the camera in such a manner as to throw as much light as possible on the grating. By holding the eye in the position later to be occupied by the photographic plate, we could easily tell when the grating was properly illuminated.

After everything was satisfactorily adjusted the lights were extinguished and the plate inserted in the camera. Great care was taken not to move any parts of the apparatus; the camera was closed, the source of light again turned on and the exposure made. It is clearly seen that in making any spectrogram, using three cells differing in length so markedly, we virtually had three different sources of light; and, consequently, the length of exposure sufficient to give comparable results on the photographic plate had to be determined by a long series of experiments. In the case of the longest cell, exposures as long as several minutes were made; while with the shortest cell only a few seconds were necessary to give good, clear spectrograms on the photographic plate.

The remaining procedure was essentially the same as that described by Jones and Anderson <sup>56</sup> and by other workers in this laboratory.

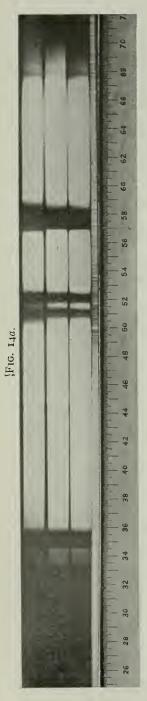
One plate will show the character of the results obtained.

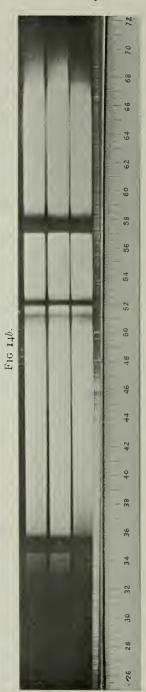
#### Neodymium Chloride in Water (see Fig. 14).

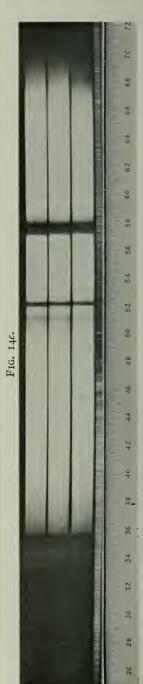
The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the spark spectrum, were 2.05, 0.0205, and 0.00401 normal, respectively; the corresponding depths of absorbing layer being 0.5 cm., 50 cm., and 250 cm.

For B the concentrations used were 1.025, 0.01025, and 0.00205 normal. The depths of layer were the same as used

<sup>&</sup>lt;sup>56</sup> Carnegie Institution of Washington, Publication 110.







in A. It is seen that the dilutions are just one-half that of the corresponding layers in A.

The concentrations of solutions used in making C were just half of those in B,—i.e., 0.512, 0.00512, and 0.00102 normal. In the entire plate, as in the dilution work, the most dilute solution is always nearest the spark spectrum.

Since very much of the finer detail, and several of the narrowest bands are lost in reproducing and printing the films, our discussion is always based upon the original photographic film. Lines will frequently be discussed which do not appear on the printed plates, but which are very clear and distinct on the photographic film.

A study of A shows complete absorption in the violet up to λ<sub>3,3,50</sub>; then slight transmission for about 50 Angström units. The faint hazy band  $\lambda_{3400}$ , and the well-defined band  $\lambda_{3450}$ - $\lambda_{3}600$  are not affected by the change in dilution. Hazy bands appear at  $\lambda_3 820$ ,  $\lambda_4 040$ , and  $\lambda_{4200}$ . Their intensities do not seem to be affected by dilution. The beautiful sharp band  $\lambda_{4275}$ , is slightly more intense in the most concentrated solution. effect of dilution, if any, on the bands λ4325, λ4440, λ4600, λ4600,  $\lambda$ 4750, and  $\lambda$ 4820 is not measurable. On the original film they appear slightly broader, but not more intense, on the third strip.

Bands which have their centres near  $\lambda_{5100}$ ,  $\lambda_{5200}$ , and  $\lambda_{5800}$ are decidedly affected by dilution; the former two appearing distinctly as independent bands in the most dilute solution, diffuse with a single broad band with the centre near  $\lambda_{5150}$ . There is the greatest change between the second and third strips (in discussing any plate strip I is always nearest the spark lines). The broadening of these bands, both of which have rather hazy edges, is fairly uniform,—i.e., they widen both towards the red and violet ends of the spectrum.

The intense band which extends from  $\lambda_5690$  to  $\lambda_5850$  is affected very markedly by dilution, the widening being almost entirely towards the red end of the spectrum. The violet edge is hardly affected, while the widening towards the red is about 50 Angström units. Here also the change in the width of the band is greatest where the change in concentration of the solution is greatest. There is a very faint band,  $\lambda 6225$ , which appears slightly more diffuse in the most concentrated solution.

The concentrations of the solutions used in B, are just one-half those of A, and it is seen that some of the smaller bands are lost, while the broader ones have split into two or more smaller bands. In this film bands near  $\lambda_{3425}$ ,  $\lambda_{3475}$ ,  $\lambda_{3520}$ ,  $\lambda_{3575}$ ,  $\lambda_{4275}$ ,  $\lambda_{4340}$ ,  $\lambda_{4450}$ ,  $\lambda_{4700}$ ,  $\lambda_{4750}$ ,  $\lambda_{4820}$ ,  $\lambda_{5100}$ ,  $\lambda_{5120}$ , show no change with dilution. The broad band  $\lambda_{5700}-\lambda_{5825}$  shows a widening of about 25 Angström units, being the only band which is changed by dilution.

C of this plate is the spectrogram of solutions twice as dilute as those of B. No band on this plate shows any appreciable change produced by dilution, except probably a slight widening of  $\lambda_{5750}$ .

We then see, from a study of this plate, that in A, bands  $\lambda_{4270}$ ,  $\lambda_{5100}$ ,  $\lambda_{5200}$ , and  $\lambda_{5750}$ , narrow with dilution, the amount of change being in the order given; that is, least in  $\lambda_{5100}$  and greatest in  $\lambda_{5700}$ . In B there is an appreciable change in only  $\lambda_{5750}$ , while in C none of the bands are affected by dilution.

! Only the two bands  $\lambda_{5275}$  and  $\lambda_{5800}$  show marked change with rise in temperature. There is a general tendency for almost all the other bands to become slightly more diffuse, although it is difficult to say that this may not be caused by general absorption. However, with bands  $\lambda_{4275}$  and  $\lambda_{5800}$  the change is a real one. Experiments made by overexposing the strips corresponding to the high temperatures, had little or no effect on the changes produced by raising the temperature. Since the development of a photographic plate depends upon the amount of light falling upon it, independent of the period of time it is falling, it is clear that the effect of general absorption could be counterbalanced by increased time of exposure.

The two bands mentioned above widened rapidly as the temperature was raised, this widening being, in both cases, almost entirely towards the longer wave-lengths.

The band  $\lambda_5800$ , in the most concentrated solutions, widened as much as 80 Angström units; while the amount of widening was directly dependent upon the concentration. It is always greater between the second and third strips. This is what we should expect, since the change in dilution between the two solutions whose spectrogram they represent, is one hundred times, while the succeeding dilution was only five times. The violet edge

of this band remains almost constant over the range of temperature studied.

The band  $\lambda_{4275}$ , a very sharp, intense band at the lower temperatures, becomes rapidly diffuse as the temperature of any solution is raised. With this band, as with the  $\lambda_{5800}$  band just discussed, the change is taking place almost exclusively on the red edge; the shading being a gradual one. This edge, the definition of which at ordinary temperature could be seen almost to I Angström unit, covers about 40 Angström units at 190°. The double band with its centre near  $\lambda_{5150}$  remains about constant in any given section; but in those bands whose width or intensity is changed by change in temperature, the change is greatest in the most concentrated solutions,—i.e., where the number of molecules is greatest.

It has been shown that with dilution three of the neodymium bands are affected, namely,  $\lambda_{4275}$ ,  $\lambda_{5150}$ , and  $\lambda_{5800}$ . Of these three the change is apparently greatest in  $\lambda_{5800}$ , next in  $\lambda_{5150}$ , and least in  $\lambda_{4275}$ . It cannot be said to be really least in  $\lambda_{4275}$ , but rather less noticeable. It is probable that the percentage change, with regard to the total width of the band, is much greater with this band than in the two preceding bands.

The change in  $\lambda_5800$  is a widening of about 60 Angström units in the most concentrated solutions, as we pass in the direction of the concentrated solutions. This widening, as in the temperature effect, is entirely towards the red end of the spectrum. The widening of the double band near  $\lambda_{5150}$  is uniform toward both ends of the spectrum. This change is appreciable only in the very concentrated solutions.

Considering a single plate, which represents the spectrogram of three different dilutions in terms of Beer's law, we see the following:

This change is greatest in Section A,—i.e., the most concentrated solution; less in B; and hardly measurable in C.

The change is greater with the acetate than with the other salts of neodymium, and is always greatest where the difference in concentration is greatest,—i.e., between strips 2 and 3.

When we consider the effect of dilution on the dissociation, we see it is in this same ratio;—i.c., there is a much greater percentage change in the relative number of molecules pres-

ent in concentrated than in dilute solutions, for a given change in dilution.

In that dilution of any solution where the relative number of molecules is greatest—the association greatest—bands  $\lambda_{4275}$ ,  $\lambda_{5150}$ , and  $\lambda_{5800}$  are widest, and the change in dilution which affects the relative number of molecules to the greatest extent, causes the greatest change in the bands. In the more dilute solutions where this change in the number of molecules is small, there is a relatively small change in the width or intensity of the bands.

A rise in temperature produces the same change upon bands λ<sub>4275</sub> and λ<sub>5</sub>800 as concentrating the solution,—that is, rise in temperature and dilution produce the reverse effect. Band  $\lambda_{5100}$ is changed by dilution and not by temperature. From these facts it seems that band \$100 may be associated with the molecules themselves, while bands  $\lambda_{4175}$  and  $\lambda_{5800}$  have more to do with the hydrated molecule. A rise in temperature would make the hydrated absorbers, or the hydrated system containing the absorbers, simpler; and, therefore, probably freer to respond in resonance to a larger number of wave-lengths. This would cause a widening of the absorption bands. Concentrating the solution, —i.e., decreasing the actual amount of solvent,—would, according to the mass law, decrease the amount of solution; and, hence, have the same effect as raising the temperature. This is exactly what is shown to be the case by the plates with bands  $\lambda_{4275}$  and λ5800.

The  $\lambda_{5100}$  band is not appreciably affected by temperature, but is changed by dilution, being widest in the most concentrated solutions.

Since temperature has little or no effect on this band, it is probable that here hydration plays very little part. Since the band widens as the number of molecules is increased, it seems to be in some way associated with the unhydrated molecules.

So far as can be seen from the photographic plates, the other neodymium bands are affected neither by dilution nor by temperature. The absorbers in this case are probably associated with the neodymium atoms or ions. THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIO-MICROMETER—NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION.

The radiomicrometer is simply a thermo-element attached to a loop of thin copper wire suspended in a magnetic field. One of the greatest difficulties in constructing this element is to obtain copper wire which is free from all magnetic metals. If perfectly pure copper wire could be found, an instrument could be constructed of almost any desired sensibility.

A very good specimen of small copper wire was furnished us by Leeds & Northrup, of Philadelphia. This wire was dipped in dilute nitric acid, and the exterior dissolved away until the wire was of proper size. The removal of the outside coating of the wire removed practically all of the magnetic material from it, this material probably being iron from the dies through which the wire was drawn.

It was not a simple matter to construct a satisfactory thermoelectric junction. The alloys used in making this junction were 90 parts bismuth and 10 parts tin, and 97 parts bismuth and 3 parts antimony. The method of making the thermo-electric junction, and of soldering it on to the ends of the loop of copper wire, we owe to Prof. A. H. Pfund.<sup>57</sup> Fine strips of the alloys were obtained in the following manner:

A few grammes of the alloy in question were fused in a vessel free from all magnetic material, and then thrown tangentially upon a clean and smooth glass plate. In this way strips of the metal were obtained of almost any desired thickness. Some were too thin to handle; those used being about 1 mm. wide, 0.01 mm. thick, and about 5 mm. in length.

The thermo-element was made by soldering an end of a strip of one of the above-named alloys to an end of a strip of the other, the whole having the form of a letter V. The two free ends of the V were soldered to the two ends of the loop of copper wire. The soldered surfaces were blackened to absorb the energy more completely. At the end of the loop of copper wire opposite the thermo-element, a light glass rod is fastened. This carries the mirror and is suspended from above by a quartz

<sup>&</sup>lt;sup>57</sup> Physic. Rev., 34, 228 (1912); Physik. Zeit., 13, 870 (1912).

fibre. The mirror employed was about 4 square mm. This entire system, consisting of thermo-element, loop of copper wire and mirror, weighed about twenty milligrammes. It was suspended by means of a quartz fibre so that the loop hung between the poles of a strong magnet. This entire system was suspended in the interior of a glass tube, the tube being closed by a ground glass stopper, and provided with suitable windows for exposing the junction and observing the mirror. The upright tube was provided with a side tube for evacuation, and by a method devised by Professor Pfund a very high vacuum could be obtained and maintained for any desired length of time. By suitably turning the ground-glass stopper in the top of the glass tube, the loop of copper wire, mirror, and, indeed, the whole system could be made to occupy any position relative to the magnets, even after the entire system had been evacuated. The whole apparatus was supported upon a levelling stand, and packed in cotton to protect it from external radiation, the thermal junction alone being exposed to the radiation in question.

The sensibility of the instrument used can be seen from the following data: It had a full period of 8 seconds; and with a candle at a distance of a metre gave a deflection of 15 cm, when the light was allowed to fall on the junction after passing through a glass window.

When the apparatus was pumped out and the radiomicrometer thus suspended in a vacuum, the deflection for a candle at a distance of a metre was 50 cm. Since glass absorbs just about half the energy emitted by a candle, our radiomicrometer, when provided with a rocket-salt window and exposed to a candle at a distance of a metre, would give a deflection of about 100 cm.

The use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy.<sup>58</sup> The radiomicrometer was used in the study of absorption spectra of solutions, rather than the grating spectrograph and the photographic plate; because the radiomicrometer enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensities. Further, the radiomicrometer, as has already been pointed out, enables us to study the absorption spectra of solutions over a much greater range of wave-lengths than the photographic method.

<sup>&</sup>lt;sup>58</sup> Physik Zeit., 13, 649 (1912).

In building a radiomicrometer that would be adapted to this work,—that is, with sufficient sensibility and with a short period, —one of the greatest difficulties encountered was to obtain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds & Northrup, of Philadelphia, and of R. W. Paul, of London. They both furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermo-electric junction already described, 59 a most sensitive radiomicrometer, which at the same time had a very short period, was built. Work with salts of neodymium and praseodymium, the results of which were recorded in the Physikalische Zeitschrift, was done with this instrument.

At the beginning of the academic year 1912–1913 the absorption spectra of solutions of a large number of salts of different metals were mapped out. The spectra of these salts were compared with the absorption of water, using the same depths of water as the water in the various solutions. It was soon found that the absorption of the solution was *less*, and in some cases *very much less* than that of the layer of water having a depth equal to the depth of the water in the solution. The depth of water in the solution and from its specific gravity.

It is obvious that the above is a very remarkable fact. The dissolved substance could not have less than no absorption of light; the assumption having been made, up to this time, that in an aqueous solution the water present absorbs just as much as pure, uncombined water. The above result is directly at variance with everything that was known at the time.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance; since the water in the solution has very different absorption from an equal amount of pure, uncombined water.

We then carried out a number of experiments in cells whose

<sup>59</sup> Physik. Zeit., 13, 651 (1912).

depths could be easily and accurately adjusted, with different substances, in the following manner: We measured the absorption spectra of a number of different substances. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more trans-The percentage transmission,—that is, the deflection of the radiomicrometer for the solution, divided by the deflection for water,—for the first-named substances, amounted to more than one hundred per cent. Pure water had a different absorption from an equal depth of water in the solution, and, since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflection for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated, are more transparent than pure water having the depths of the water in the solutions in question. Solutions of non-hydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution.

It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure, uncombined water. To test this quantitatively the following procedure was adopted:

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell, set to a depth of say 2 mm. Some of the same solution was then placed in another cell, set to a depth of say 1 mm. Light of given, known wave-length was then passed through

the one solution and the deflection noted. Light of this same wavelength was then passed through the other solution, and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced when the shallower solution was in the path of the light, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm. This process was repeated for the different parts of the spectrum, changing the wave-length of light from reading to reading by only a small amount. Light of any given wave-length was always passed through the one solution, and then, at once, through the other solution of a different depth. The object in using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower.

From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say 21 cm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep could also be calculated. Water was then introduced into the two cells, and these cells so adjusted that the difference in the depth of the two was exactly equal to the depth of the water in the layer of the solution which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave-length of light; and then, at once, the deflection when the light was passed through the *more shallow* layer of water. The deflection for the deeper layer was divided by the deflection for the more shallow layer. This operation was repeated for the various wave-lengths of light in the manner just described. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in question.

The above results for the solution are plotted as one curve, and those for water having the same depth as the water in the solution as another curve, wave-lengths being abscissæ and transmission ordinates. A comparison of the two curves shows at once whether water in the free, uncombined condition, or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the more shallow, and, similarly, by those for water, are also given in the following tables. These are the data from which the accompanying curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light. We were limited to those substances that are both colorless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

We selected for these substances with little or no hydrating power salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. We selected for the salts with large hydrating power calcium chloride, magnesium chloride, and aluminium sulphate. These salts were shown by the earlier work in this laboratory, which was done shortly after Jones proposed the solvate theory of solutions, using the freezing-point method, to be among the most strongly hydrated substances with which we are familiar.

It will be seen from the following data that two depths of layer of each solution of every substance investigated were employed. The object of this was to bring out the two most important water-bands in the region of the spectrum investigated. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water-bands, would not bring the other out in the way desired. By using the two depths of solution and studying each of them in the manner described above,—that is, by the differential method,—we were able to investigate both of the water-bands as produced, on the one hand, by the pure solvent, and, on the other, by the solution.

# THE CHEMISTRY OF HUMUS, WITH SPECIAL REFERENCE TO THE RELATION OF HUMUS TO THE SOIL AND TO THE PLANT.\*

### S. L. JODIDI, B.S., Ph.D.

[This article is largely based upon the work conducted during the last six years by the writer while he was connected with the Michigan and Iowa Agricultural Experiment Stations.]

UP to a few years ago the generally-accepted idea was that humus is made up of but a few organic compounds, chiefly acid in their nature. However, the more recent investigations have thrown enough light upon the chemical nature of humus or humus organic matter in the soil to demonstrate that it is a very complex substance which, in addition to the dark-colored humin bodies, contains a large number of organic compounds displaying acid, basic, neutral, and amphoteric character.

Considered from a modern point of view, the solution of the humus problem consists, first of all, in finding out all of the compounds—the simple bricks—of which humus is made up, as well as the proportion in which those compounds are mostly present in humus, and, further, to ascertain just which of the compounds in question are, as such, present in humus and which of them constitute parts of one or several more complex bodies.

What we at present designate as soil organic matter or humus will thus, in the course of time, by modern methods of research, be separated into a number of bodies of well-known composition and structure.

Whereas a part of the above problems may now be considered as accomplished—the results in question will be mentioned later—it may be worth while to show here that in some measure the development of the idea of the chemical nature of humus stands in a certain relation to the development of the chemistry of carbohydrates and proteins out of which humus is being formed in the soil.

For centuries mankind knew only cane-sugar or saccharose, which was originally extracted exclusively from the sugar-cane. The same sugar was later discovered in the sugar beet (Marg-

<sup>\*</sup> Communicated by the author and published by permission of the Secretary of Agriculture.

graf, 1747), sorghum, maple tree, and other plants. In addition to this sugar, there were discovered, also, lactose in the milk (Bartoletti, 1619), glucose (Lowitz, 1792), fructose (Dubrunfaut, 1847), etc., so that at present we know a considerable number of sugars in the form of bioses, trioses, tetroses, etc., up to nonoses,—i.e., sugars which contain in their molecule from two to nine carbon atoms respectively, and which in part occur as such in nature, the pentoses and hexoses and the corresponding polysaccharides being the most important ones.

As was demonstrated by many researchers, such sugars and, generally speaking, carbohydrates, when treated with acids or alkalies, vield brown or black humin substances, whose physical and chemical properties remind one of soil humus to such a degree that the artificial and natural products were considered by some as closely related,2 by others even as identical.

When, however, dilute acids are applied, the carbohydrates vield a number of well-defined intermediary products. Thus the polysaccharides furnish, first, monosaccharides; these latter yield organic acids, etc. For the raffinose, e.g., we have: Raffinose (melitriose) → melibiose (+ d-fructose) → d-glucose + galactose. The monosaccharides obtained can yield, e.g., lactic4 acid, butyric<sup>5</sup> acid, alcohol, citric acid, etc., depending upon the conditions of fermentation.

<sup>5</sup> Fitz, Ber. d. chem. Ges., vol. 17, p. 1188 (1884); Grillone, Ann. (Liebig), vol. 165, p. 127 (1872); Winogradsky, Chem. Centralbl., 1902, ii, p. 709.

<sup>&</sup>lt;sup>1</sup> Malaguti, Ann. (Liebig), vol. 17, p. 52 (1836); Berzelius, "Lehrbuch d. Chemie." 3. Aufl., 1839, 8. Bd.; Conrad u. Guthzeit, Ber. d. chem. Ges., vol. 18, p. 439 (1885), vol. 19, p. 2850 (1886); Sestini, Gaz. Chim. It., vol. 10, pp. 121, 355; Grote u. Tollens, Ann. (Liebig), vol. 176, p. 181 (1875), vol. 202, p. 226 (1880); Péligot, Ann. Chim. Phys. [2], vol. 73, p. 208; Mulder, Ann. (Liebig), vol. 36, p. 243, Chemie der Ackerkrume; O. Schmiedeberg, Arch. expt. Path. und Pharmakol., vol. 39, p. 1 (1897); Hoppe-Seyler, Zeit. physiol. Chem., vol. 13, p. 66 (1889); Samuely, Beitr. chem. Physiol. und Path., vol. 2, p. 355 (1902).

<sup>&</sup>lt;sup>2</sup> Sostegni, Landw. Vers.-Stat., vol. 32, p. 9 (1885); André, Bull. Soc. Chim. [3], vol. 21, p. 497 (1899); Eggertz, Chem. Centralbl., 1889, p. 343. Scheibler u. Mittelmeier, Ber. d. chem. Ges., vol. 22, pp. 1682 and 3118.

<sup>&</sup>lt;sup>4</sup> Pasteur, Ann. Chim. Phys. [3], vol. 2, p. 257 (1842); Buchner u. Meisenheimer, Ann. (Liebig), vol. 349, p. 124 (1906); Henneberg, Oest.-Ung. Zeitschr. Zuckerind. u. Landw., vol. 30, p. 1065 (1901).

<sup>&</sup>lt;sup>6</sup> Pasteur, Ann. Chim. Phys. [3], vol. 58, p. 323 (1860); Dubrunfaut, Compt. rend. Acad. Sc., vol. 42, p. 945 (1856); Jodblauer, Zeitschr. Verein. d. Zuckerind., vol. 38, p. 344 (1888); Schunk, Ann. (Liebig), vol. 66, p. 174 (1847).

So far as proteins are concerned, it was first thought that they have a constant composition and definite constant <sup>7</sup> properties. The modern researches revealed the fact that the various proteins have different chemical composition and structure, and accordingly they show different physical, chemical and physiological properties.

While the number of amino <sup>8</sup> acids out of which the protein molecule is chiefly built up is limited, the number of possible proteins is by far greater, for the reason that proteins can differ from each other either because they contain different amino acids or varying amounts of them, or because the amino acids can in the protein molecule follow each other in a different order, or may be linked with one another in a different way. Whatever the composition and structure of the proteins is, their gradual decomposition leads (through the stages of albumoses, propeptones, peptones) to diamino and monoamino acids. And it is just the latter compounds which play a rôle in the formation of humin substances.

A number of investigators <sup>9</sup> have found that proteins, when treated with acids, yield humus-like bodies. A further study of the phenomenon involved showed that it is particularly the diamino acid lysine <sup>10</sup> and the monoamino acids tryptophane <sup>11</sup> and tyrosine (and glucoseamine) that participate in the production of the melanoidins. <sup>12</sup>

<sup>&</sup>lt;sup>7</sup> A. Kossel, Ber. d. chem. Ges., vol. 34, p. 3245 (1901).

<sup>&</sup>lt;sup>8</sup> The discovery of leucine in cheese by Proust in 1818, and of tyrosine by Liebig in 1846, followed by discoveries of other amino acids, the number of which was more recently increased, thanks to the researches of E. Fischer and his school. A complete enumeration of them (including some synthetic amino acids) is given in Fischer's "Untersuchungen über Aminosauren. Polypeptide und Proteine," Berlin, 1906, pp. 19–23. See, also, E. Abderhalden and A. Weil, Zeit. physiol. Chem., vol. 81, p. 207 (1912).

<sup>&</sup>lt;sup>o</sup> Mulder, Journal für practische Chemie, vol. 21, p. 343 (1840); "The Chemistry of Vegetable and Animal Physiology," translated by D. P. H. Fromberg, Edinburgh and London, 1849, p. 153; O. Schmiedeberg, Archiv. exper. Pathol. u. Pharmakol., 39 (1897); Panzer, Zeit. physiol. Chem., vol. 33, p. 131 (1901).

<sup>&</sup>lt;sup>10</sup> Zeit. physiol. Chem., vol. 33, p. 355 (1901).

<sup>&</sup>lt;sup>11</sup> Hopkins and Cole, *Jour. Physiol.*, vol. 27, p. 418 (1901), vol. 29, p. 451 (1903).

<sup>&</sup>lt;sup>12</sup> F. Samuely, "Ueber die aus Eiweiss hervogehenden Melanine," Hofmeister's Beiträge, vol. 2, p. 355 (1902).

In connection with lysine, Hart <sup>13</sup> made the interesting observation in Kossel's laboratory that when proteins are hydrolyzed with acid in the presence of salts, *e.g.*, sodium chloride, they yield less humin substance and more lysine and ammonia; but when they are hydrolyzed with acid alone, they yield more humin substance and less lysine and ammonia.

While the humification in the soil of carbohydrates and proteins contained in plants, because of secondary influences, may in some measure represent a more complicated process than is the formation of melanoidins out of those substances when they are treated in the laboratory with acids or alkalies, yet it seems safe to state that plants containing proteins rich in tyrosine, tryptophane, lysine and glucoseamine will *ceteris paribus* yield more humus than plants poor in these compounds. On the other hand, protein-holding vegetable matter with a definite percentage of the amino acids mentioned may, on humification, yield varying amounts of humin substances, depending upon the conditions prevailing in the soil.

Inasmuch as carbohydrates and proteins form the bulk of vegetable and animal matter out of which humus-like substances are generally produced in the soil, it is now, in the light of our present knowledge, easy to grasp why humus has quite a complex chemical nature, just as the various carbohydrates, proteins, and their degradation products possess it in a greater or lesser degree.

· However, the early investigators into the nature of humus, such as Berzelius, <sup>14</sup> Detmer, <sup>15</sup> Braconnot, <sup>16</sup> Malaguti, <sup>17</sup> Terreil, <sup>18</sup> and especially Mulder, <sup>19</sup> with a considerable number of workers who followed him, maintained that humus consists of but a few simple organic bodies which are chiefly acid in their nature (or at least can be converted into acids by treatment with alkalies), and which are closely related to each other. According to Mulder, *e.g.*, the ulmic acid, the first stage in decomposition of organic matter, is gradually converted into humic acid, geic acid,

<sup>&</sup>lt;sup>13</sup> "Ueber die quantitative Bestimmung der Spaltungsproducte von Eiweisskörpern," Zeit. physiol. Chem., vol. 33, p. 347 (1901).

<sup>14</sup> Loc. cit.

<sup>&</sup>lt;sup>15</sup> Landw. Versuchsstationen, vol. 14 (1871).

<sup>16</sup> Ann. Chim. Phys., vol. 12, p. 191 (1819).

<sup>&</sup>lt;sup>17</sup> Ann. Chim. Phys. [3], vol. 54, p. 407 (1858).

<sup>&</sup>lt;sup>18</sup> Bulletin de la Soc. chim. [2], vol. 44, p. 2 (1885).

<sup>19</sup> Loc. cit.

apocrenic and crenic acid, in the order named, all of which consist of but three elements, namely, of carbon, hydrogen, and oxygen. This conception of Mulder and contemporary writers may in part have been due to the fact that protein was at that time considered as being of constant definite composition, that the number of carbohydrates and of their disintegration products known was comparatively limited (which was also true of the protein products), and, last but not least, that the methods of research in the organic and biological chemistry were inadequate.

Since, as practice has shown, humus is of such vital importance to plant life that soils are in some measure valued according to their humus <sup>20</sup> content, it may not be out of place once more briefly to discuss the possible nature of the bodies resulting through decay of organic materials in the soil.

When pure proteins are subjected to the influence of enzymes or to the activity of micro-organisms, they are first hydrolyzed chiefly to diamino acids and monoamino acids. The resulting primary amino acids are, especially under the influence of microbes, subjected to secondary changes which lead to the formation of humin substances, of fatty and hydroxy acids, of phenols, basic substances, etc. Thus, the splitting off of CO<sub>2</sub> from the diamino acids as well as of the NH<sub>2</sub> group from the monoamino acids leads to the formation of amines and acids respectively, as illustrated by the following equations:

<sup>20</sup> I wish to call attention to the great usefulness of the shaking machine which, upon recommendation of the writer, was introduced in the Michigan and Iowa Agricultural Experimental Stations. The shaker, which deserves to be used more generally in experiment stations, colleges, and elsewhere, can successfully and advantageously be applied practically in all cases where hand-shaking is required. The shaker is an excellent apparatus for preparation of extracts of all kinds, especially of humus extracts, for dissolving various substances, for ammonia determinations according to Schlösing's

In the case of nucleoproteids there result, in addition to protein products, purine derivatives and pyrimidine bases.

Equally when carbohydrates are subjected to the influence of enzymes and bacteria, they are, as the result of primary hydrolysis, first split into smaller molecules, still representing carbohydrates, which latter are then further decomposed, through fermentation, to alcohol, organic acids, etc.

In a similar manner the fats are split, under the influence

of the agencies mentioned, into fatty acids and glycerol.

There is no reason to assume that the proteins, nucleoproteids, carbohydrates, and fats contained in the remains of vegetable and animal life, when subjected in the soil to the action of similar agencies, should not give the same decomposition products which result in the case of pure proteins, nucleoproteids, carbohydrates, and fats.

Now, broadly speaking, humus is bound to contain qualitatively the same constituents or, rather, elements as the remains of vegetable and animal life out of which it was formed. It is, however, plausible that the quantitative composition of humus which constantly undergoes changes in the soil will be different from what it was in the organic materials, for a number of reasons. In the first place, the comparatively easily soluble cleavage products are leached out of the soil organic matter, while the less soluble compounds accumulate in the humus. Equally, the chemically more resistant primary cleavage products will accumulate in the humus, while the less resistant bodies will undergo secondary decomposition. For this very reason fresh humus must contain more of the primary cleavage products, whereas old humus is bound to contain more of secondary decomposition products.

While the amount and nature of humus formed in the soil

method, for estimation of solubility of substances, etc. In all such cases the employment of the shaker means saving of time, labor, and attention, at the same time affording a means for obtaining uniform results. There are a variety of shaking machines on the market. I have used with satisfaction the electrically-driven shaker as shown on page 418 of the Scientific Materials Company's catalogue for 1912, or on page 333 (No. 4589) of the catalogue of Eimer & Amend for 1905.

For instance, the extraction of humus from soils, which, according to the method of the Assoc. Off. Agr. Chem., requires 24 hours, can be accomplished in the shaker within some three hours. primarily depends upon the quantity and character of the organic materials which undergo humification, it should be borne in mind that also other factors, like temperature, moisture, aëration of the soil, presence of certain chemical substances (salts, acids, etc.), as well as character and quantity of microbes contained in the soil, have more or less influence upon the nature of humus produced.

Whereas, with the full access of air and with suitable temperature and moisture conditions the process of eremacausis leads to a complete oxidation of the elements contained in humus materials whereby carbon is oxidized to carbon dioxide, hydrogen to water, nitrogen to nitric acid (through the stage of ammonia) and sulphur to sulphuric acid, the process of putrefaction leads to a number of intermediary products.

It happens comparatively seldom that in nature humification of organic materials takes place by one of the above processes to the exclusion of the other. More frequently both eremacausis and putrefaction set in, and while a part of the humus is entirely oxidized, the rest of it is decomposed to products a number of which have in the last few years been extracted from soils and identified as to their chemical nature. The results of this latter work show that humus—using this word in its widest sense—is of a very complex nature, consisting, as it does, of a large number of compounds. Contrary to the findings of earlier writers (see p. 568), humus contains, in addition to carbon, hydrogen, and oxygen, also nitrogen, sulphur, and phosphorus; it contains acids of well-known composition and constitution, like monohydroxystearic, 21 dihydroxystearic, oxalic, succinic, acrylic, saccharic; it contains bodies basic in nature, like diamino 22 acids (Kossel's hexon bases), purine 23 bases and amines;24 it is made up of a variety of "neutral" compounds like hydrocarbons, 25 esters,

<sup>&</sup>lt;sup>21</sup> Schreiner and Shorey, Bul. Nos. 53 and 74, Bureau of Soils, U. S. Dept. Agr.; *Journal Amer. Chem. Soc.*, 32, 1674 (1910); Original Communications, Eighth Intern. Congress Appl. Chem., vol. xv, p. 247.

<sup>&</sup>lt;sup>22</sup> Jodidi, S. L., Tech. Bul. No. 4 (1909), Mich. Agr. Expt. Station; Research Bul. No. 1, Iowa Agr. Expt. Sta.; Jodidi and Wells, Research Bul. No. 3, Iowa Agr. Expt. Sta.

<sup>23</sup> Loc. cit.

<sup>24</sup> Loc. cit.

<sup>&</sup>lt;sup>25</sup> Shorey, E. C., Original Commun., Eighth Intern. Congress Appl. Chem., vol. 15, p. 248 (1912).

aldehydes, as well as of bodies amphoteric in their nature, like amino <sup>26</sup> acids, etc.<sup>27</sup> Moreover, there can be very little doubt but that the number of definite organic compounds which can be extracted from soil organic matter will considerably be increased within the next few years. It is, however, a matter of course that humus of any one soil will contain only a part of the constituents enumerated above or yet to be found, and will in various soils differ in its composition, just as the various proteins, carbohydrates, and fats occurring in decaying organic materials show differences in their composition and constitution.

It may not be amiss to mention here that of the compounds found in soil organic matter the amino acids and acid amides play a prominent rôle because of the fact that they are contained in predominant proportions in acid extracts of soils, and for the further reason that they represent an important source for the production in the soil of ammonia,<sup>28</sup> and hence of nitrates.

Taking into consideration that certain constituents—the ten well-known elements—are absolutely indispensable for plant life, it is easy to understand why humus is called by many the life of the soil. Not only does it contain most of the elements which were recognized to be necessary for plant life, like nitrogen, phosphorus, sulphur, etc., but, what is of equally great importance, it affords a means for rendering more of the necessary inorganic elements available. The carbon dioxide, which is gradually being formed through oxidation of a part of the humus carbon, represents in combination with water a powerful agent for dissolving rocks and making the elements potassium, magnesium, calcium, and others contained in them available. Equally, as is known, the nitric acid and sulphuric acid, which result through oxidation of the elements nitrogen and sulphur present in humus, are strong agents for dissolving the indispensable elements out of the rocks.

<sup>&</sup>lt;sup>26</sup> Jodidi, S. L., *Journal Amer. Chem. Soc.*, vol. 32, p. 396 (1910), vol. 33, p. 1226 (1911), vol. 34, p. 94 (1912); Schreiner, O., and Shorey, E. C., *Journal Biol. Chem.*, vol. 8, p. 381 (1910); Robinson, C. S., Tech. Bul. No. 7, Mich. Agr. Expt. Sta.; *Journal Amer. Chem. Soc.*, vol. 33, p. 564 (1911).

<sup>&</sup>lt;sup>27</sup> A good account of the compounds extracted from soils is contained in Original Commun., Eighth Intern. Congress Appl. Chem., vol. 15, pp. 248–250.

<sup>&</sup>lt;sup>28</sup> Jodidi, Kellogg and Snyder, Research Bul. No. 9, Iowa Agr. Expt. Station; Jodidi, Journal of The Franklin Institute, vol. 175, p. 245 (March, 1913); *Ibid.*, p. 483 (May, 1913); Original Communications, Eighth Intern. Congress Appl. Chem., vol. 26, p. 119 (1912).

that way converting rocks and rocky land into fertile, arable soil.

It is also well known that humus improves the physical condition of the soil. It increases, for instance, its capacity to hold water, to retain valuable nitrogenous constituents, to resist corrosion; it binds the particles of sandy soils; it makes clayey soils friable, increasing at the same time the capacity of the soil to absorb the sun's rays and making the soil temperature more uniform. In other words, humus makes the soil a more habitable and suitable home for the performance of the life functions of plants.

Thus we find the humification process inserted into the chain of Nature's cycles as a most necessary link, without which the perpetual continuance of plant life cannot very well be conceived. Again, man's food, whether of vegetable or animal origin, is composed chiefly of proteins, fats, carbohydrates, and some mineral substances, all of which are contained in the plant and animal body. Animal life, however, is, in the last analysis, based upon the presence of plants, the digestion and assimilation of which gives the material for the formation in the animal body of its organs and tissues. Again, the plants need for their life certain elements which are present in humus. Here we have, then, a cycle in which physical life of man, as well as the existence of the animal and vegetable kingdoms, is brought into close connection with humus. So close is this relation that conditions indispensable for life are also necessary for decomposition of humus materials. and that extremes excluding life render also decomposition impossible. There is practically no plant life in Arctic regions or throughout the winter, and there is no decomposition under the same conditions. On the other hand, plant life is luxurious in the tropics. There, too, decay is very rapid. The plant and animal kingdoms need for their life air. The same air is indispensable for decomposition. Equally, neither plant life nor decomposition of organic substances is possible without water. The above coherence means that in the process of humification Nature has a powerful means for the utilization of vast amounts of waste materials for purposes of life.

Office of Physiological and Fermentation Investigations, Bureau of Plant Industry, U. S. Department of Agriculture. Safety of Life at Sea.—Recommendations of the committee appointed by the Secretary of Commerce for the use of the American delegation to the International Conference on Safety of Life at Sea to be held in London during the present month:

I. That efficient apparatus for the radio communication be required on all ships in foreign trade which carry 50 persons or more (passengers or crew, or both combined), navigating the ocean between ports more than 200 nautical miles distant from one another.

2. That apparatus, to be deemed efficient, must transmit messages with sufficient power to be received by day over sea at a distance of at least 100 nautical miles by a ship equipped with apparatus equal

to that of the transmitting ship.

3. That an auxiliary power supply should be provided, independent of the vessel's main electric power plant, which will enable the sending set for at least four hours to send messages over a distance of at least 100 nautical miles by day.

4. That (a) two first-grade operators should be required on all such ships maintaining a constant service, also on all such ships

carrying 100 or more passengers.

(b) One first-grade and another first- or second-grade operator should be required on all other such passenger ships.

(c) One operator (first or second grade) and one cargo operator

or watcher should be required on all such cargo boats.

The recommendations of the committee are based not only on the laws of the United States but also in principle on the London International Convention and the laws of Canada and Australia. The laws of Canada and Australia do not specifically require a constant wireless watch on cargo boats, but authorize the admin-

istrations of those colonies to impose that requirement.

The second operator or watcher on a cargo boat will rarely be required for the safety of his ship or the crew of which he is a member. The constant watch is to be maintained almost entirely for the purpose of enabling the master of the cargo boat to be at all times in a position to receive radio distress calls and to render the assistance within his power. The proposition, accordingly, is in the interests of the safety of the seafaring world, and is, in effect, a tax upon the owners of such cargo boats for the promotion of the safety of others.

The committee comprised E. T. Chamberlain, Commissioner of Navigation, Chairman; W. H. G. Bullard, Captain, U. S. Navy, Superintendent Naval Radio Service; C. McK. Saltzman, Major, U. S. Army, Assistant to Chief Signal Officer; Jno. Q. Walton, Constructor, Revenue-Cutter Service; Frederick A. Kolster, Bureau

of Standards.

Silver Solder. Anon. (Brass World, ix, 9, 306.)—Silver solder is far superior to spelter solder for brazing metals, as it melts more readily and forms a stronger and tougher joint. As its advantages are appreciated it is becoming more and more extensively used.

#### A NEW AUTOMATIC FIRE ALARM.\*

BY

#### F. A. J. FITZGERALD,

FitzGerald and Bennie Laboratories, Niagara Falls, N. Y. Member of the Institute.

So MUCH has been published in recent years in regard to the enormous annual loss from fires that nearly every one knows the magnitude of the problem and the importance of adequate fire protection. One result has been the extension of the use of sprinkler systems, and it is unquestionable that these have greatly reduced the fire losses. However, for obvious reasons there are many places where the installation of sprinkler systems is not feasible and where, nevertheless, the use of some form of fire protection is desirable. Moreover, even where the sprinkler system is in use it is important that an alarm of fire should also be given, and if this can be made automatic—so much the better.

For more than a year a very ingenious device for use as an automatic fire alarm has been the subject of considerable research work in this laboratory, and it is believed that a detailed description of it and its method of manufacture will be of interest.

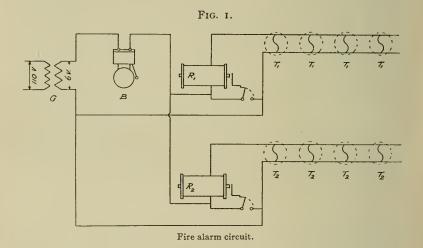
#### GENERAL PRINCIPLE.

The fire alarm is manufactured by the General Fire Alarm Corporation, and is the invention of Mr. Eugene Garretson. It consists in the use of a thermoscope in which the active element is a substance having a negative temperature coefficient of electrical resistance. The thermoscope forms part of an electric circuit, which also contains an alarm gong and indicating device, but has such a high resistance under normal conditions that the current passing through the circuit is not sufficient to work the alarm. If, however, the temperature of the air surrounding the thermoscope rises to a certain degree the electrical resistance drops so as to permit the passage of sufficient current to give the alarm.

In Fig. 1 is shown the wiring diagram of a fire detector for two stations. The source of the current for the circuit is shown

<sup>\*</sup> Communicated by the author.

at G, the alarm gong at B, and relays with drops at  $R_1$  and  $R_2$ , corresponding to the two stations protected with the series of thermoscopes  $T_1$  and  $T_2$  respectively. If the circuits are traced it is seen that they are complete only through the normally high resistance thermoscopes, and consequently the current is not sufficient to trip the relays nor to release the mechanical gong. Suppose, however, that a fire occurs in the room where the thermoscopes  $T_1$  are installed, the resistance of one or more of these will be sufficiently lowered to permit the passage of current that will trip the relay  $R_1$ , thus indicating where the fire is and closing absolutely the alarm gong circuit.



#### THE THERMOSCOPE.

So far as the general principle of the invention is concerned, it is plain that a large number of substances might be used as the sensitive element of the thermoscope,—in fact, any substance with a negative temperature coefficient; but for practical purposes the substance should have other qualities than the mere possession of a negative temperature coefficient.

A thermoscope of this kind should have the following characteristics:

(1) A very high resistance at ordinary temperatures.

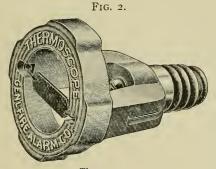
(2) A large temperature coefficient, so that a small increase in temperature produces a large decrease in resistance.

- (3) Its heat capacity should be small, so that as the resistance drops the increase in current, even though a very small one, passing through the thermoscope tends to heat it, and thus greatly increases the sensitiveness of the detector as the critical temperature is approached.
- (4) Its characteristics should be permanent under all conditions to which it is apt to be exposed.

One of the best of the substances which have been found for this purpose, and to which Mr. Garretson applies the general name *thermitite*, is a preparation of silver sulphide.

#### ELECTRICAL PROPERTIES OF THERMITITE.

Before considering the properties of thermitite as investigated in this laboratory it will be well to describe the thermo-



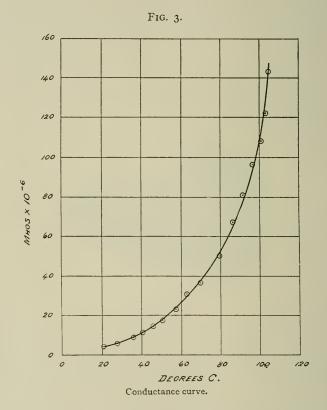
Thermoscope.

scopes as made for use in practice, as most of the tests which will be described were made with these. In Fig. 2 we have a cut showing a thermoscope, actual size. The mount is made of glazed porcelain and carries a threaded brass shell which screws into a socket just as in the case of an ordinary incandescent lamp. The thermitite strip has copper wires fused to its ends, and these are soldered to the contacts.

If one of these thermoscopes is put in a circuit with a small six-volt tungsten lamp and three dry cells connected in series the lamp will not light up; but if a lighted match is held under the *thermitite* the lamp almost instantly begins to glow with full candle-power. If the match is removed and the piece of *thermitite* cooled in any way the lamp is extinguished.

This, however, would not be the method when using the thermitite for a fire alarm, since that substance is an electrolyte, and, even though a solid, electrolytic changes might be expected were a direct current used in the circuit. That electrolysis does occur may be shown by the following experiment:

A piece of thermitite provided with silver electrodes was placed in a direct-current circuit for some time. Then the ther-

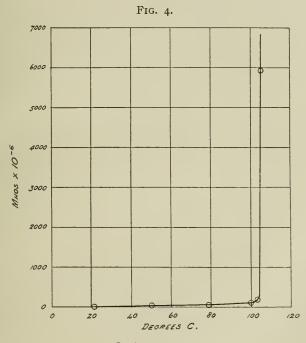


mitite was cut out of the circuit and the electrodes connected to the terminals of a sensitive galvanometer which was immediately deflected, showing the generation of a current in the opposite direction to that which had been passed through in the direct-current circuit.

The experiment clearly shows a phenomenon-like polarization in an ordinary electrolytic cell. Obviously, then, in the use of

thermitite as a thermoscope an alternating current must be used. It also indicates the necessity of using an alternating current in any attempt at making measurements of the electrical resistance of the thermoscope. The study of the behavior of silver sulphide as an electrolyte must be reserved for a future paper, as the work on it is not yet complete, for it was necessary first to develop a commercial thermoscope rather than make a complete investigation of the electrical properties of the thermitite.

An investigation of the change of resistance of thermitite



Conductance curve.

with temperature has been made with the express object of studying its action when used as a thermoscope. For this purpose a bridge was used, the current being supplied by a small induction coil and a high-resistance telephone receiver taking the place of a galvanometer. The thermoscope was immersed in an oil-bath heated by a coil of wire through which a current was passed. A rheostat was used to regulate the current so that the temperature of the oil-bath, which was kept thoroughly stirred,

could be controlled. The result of one of these experiments is given in the curves of Fig. 3 and Fig. 4, where the abscissæ are degrees Centigrade and the ordinates are mhos  $\times$  10<sup>-6</sup>.

Referring to Fig. 3, the curve shows the increase in conductance from  $4.3 \times 10^{-6}$  mhos at  $21^{\circ}$  to  $143 \times 10^{-6}$  mhos at  $104^{\circ}$ . Then a very abrupt change was observed, for at  $105.5^{\circ}$  the conductance was  $5880 \times 10^{-6}$  mhos. This sudden change is shown best in the curve of Fig. 4, which is from the same observations, but plotted on a different scale.

Now it is not pretended that the curves shown in Fig. 3 and Fig. 4 represent the true conductance of the thermoscope at the corresponding temperatures. The temperatures are those of the oil-bath and not of the *thermitite* itself, which may be higher, due to the passage of the current. The important point, considering the use of the *thermitite*, is that at a certain temperature in an electric circuit an enormous increase in its conductivity occurs.

In order to form some idea of how the thermoscope behaves when heated in air a different test is used. The circuit is similar to that shown in Fig. 1, and the thermoscope is put in an oven heated by means of a coil of nichrome wire through which a current controlled by a rheostat is passed. The temperature of the oven is raised until the alarm is given. This is found to be at approximately 80° C. It is obvious from this test that the temperature at which the alarm is given is not the temperature of the thermitite, but merely that of the surroundings. This may be seen from the following calculations. In order to trip the drop of the 80-ohm relay a current of 0.04 ampère is required. The e.m.f. of the circuit is 6 volts, consequently the resistance of the circuit at the moment the relay works is

$$\frac{6}{0.04}$$
 = 150 ohms,

but the resistance of the relay is 80 ohms, consequently that of the thermoscope is only 70 ohms. The oil-bath test showed that at 80° the resistance of the thermoscope was 19,000 ohms, so it is plain that its temperature when the alarm is given is very much higher than that of the surrounding air. This, of course, is due to the heating effect of the current. Here we have an explanation of the great sensitiveness of the thermoscope, for it

does not simply depend upon the heating effect of the air to cause it to give the alarm. Indeed, it would be more accurate to say that the thermoscope fails to give an alarm because of the cooling effect of the surrounding air, and that when this cooling effect is removed the thermoscope becomes a good conductor and turns in an alarm.

#### MANUFACTURE AND TESTING.

The process of manufacturing the thermoscopes is simple. The thermitite is made in sheets 0.5 mm. thick, and from these oval-shaped pieces 10 mm. long and 5 mm. wide are punched out. Short pieces of No. 26 (B. and S. gauge) copper wire are fused to the ends of these oval pieces, and they are then put in the porcelain mounts.

Every batch of thermitite is tested by finding the oven temperature at which the thermoscopes made from it ring in the alarm. The thermitite is also tested in an oven heated to 65° C. to make sure that even at temperatures near the critical one it will not break down. Finally, all thermoscopes are mounted in large testing boards and kept under observation for at least one month to discover if any defects develop.

#### FIRE TEST.

The tests for practical work are made as follows: In a room fitted with the thermoscopes a cone made of asbestos board is moistened with about 50 c.c. of alcohol, placed on the floor under a thermoscope, and the alcohol ignited. This is quite sufficient to give the alarm, although a dial thermometer mounted beside the thermoscope fails to show more than a rise of 5 degrees C. in the temperature, nor after repeated tests has the slightest effect been observed on the varnish with which the wooden ceiling of the room is coated. No doubt, if the asbestos cone was not placed directly under the thermoscope it would be necessary to use a larger quantity of alcohol, but the test as performed shows that before the hot air about the thermoscope can even scorch varnish or cause a dial thermometer to register more than a few degrees rise in temperature the alarm is given.

Vol. CLXXVI, No. 1055-41

#### PERMANENT CHARACTER.

In order to find out if the thermoscopes were permanent, some were mounted out of doors, where they would be exposed to all conditions of weather, with entirely satisfactory results. To test resistance to the action of chemicals several thermoscopes were mounted on the ceiling of our chemical laboratory where they are exposed to the acid fumes, etc., characteristic of such a room, and no deterioration has been observed.

#### CONCLUSION.

As a result of the study of the thermoscopes it appears that for use as a fire alarm they are highly satisfactory for several reasons. They are extremely sensitive, because the immediate cause of the heating of the thermitite is the electric current of the circuit, and this is prevented simply by the cooling effect of the surroundings under normal conditions. Any heating of the surroundings not only raises the temperature of the thermitite by the heat which these give off, but at the same time increases the flow of current and consequently increases the heating effect. When the resistance is diminished one-half the current is doubled, and, since the heating effect is proportional to the product of the square of the current and the resistance, the heating effect is doubled. In fact, the system might be described as being always in a state of unstable equilibrium.

The construction of the whole system is extremely simple, being practically equivalent to an ordinary electric bell equipment with the thermoscopes replacing the push-buttons. The thermoscopes themselves are so simple in construction that they can be treated much as are incandescent lamps. Thus, enclosed in a suitable cage they may be attached to extension cords and put in places otherwise difficult to protect, such as in the cargo stowed in the holds of ships.

The tests of the *thermitite* show its permanent character. Outside of mechanical breakage the only possibility of failure is in the direction of a lowering of the electrical resistance, which would automatically indicate that there was trouble at that point.

Finally, before closing it may be of interest to note that a new use of the thermoscope as a detector of hot bearings is at present the subject of further research.

## THE TWELFTH INTERNATIONAL GEOLOGICAL CONGRESS

R. A. F. PENROSE, JR.\*

The meeting of the Twelfth International Geological Congress was held in Toronto, Canada, August 7–14, 1913. Before and after the meeting numerous geological excursions were taken by the members of the Congress in various parts of Canada, while during the meeting short excursions were taken in the vicinity of Toronto. The excursions before and after the meeting, however, were often of considerable length, the different trips covering most of Eastern Canada and extending through Western Canada as far as the Pacific Coast and the Yukon Territory. Some of the excursions began before the middle of July and others lasted until after the middle of September, so that, though the actual meeting at Toronto lasted but seven days, the movements of the Congress lasted over two months. There were in all over thirty different excursions.

The various excursions were under the guidance of Canadian geologists familiar with the regions traversed. They were excellently conceived and carried out, every provision was made for the comfort of the members, and the opportunity to see a great deal of geology in a short time and under most advantageous conditions was remarkable. Special guide-books for many of the excursions were published by the Canadian geologists and were remarkably comprehensive in their scope; in fact, they were textbooks of the geology of the regions traversed. The excursions were so arranged that the geologists coming from Europe and other places to the East could see Eastern Canada before coming to Toronto, and, after attending the general meeting at Toronto, could proceed westward on the excursions in that direction.

The proceedings of the Congress at Toronto were full of interest to all who attended them. The honorary president of the Congress was the Governor-General of Canada, the Duke of Connaught; the president was Prof. Frank D. Adams, of McGill

<sup>\*</sup> Mr. Penrose and Mr. E. V. D'Invilliers were official delegates of the Institute.

University, Montreal; the general secretary was R. W. Brock, Director of the Geological Survey of Canada; and the secretary was W. Stanley Lecky. The meeting was opened with speeches of welcome by the Right Honorable Sir Charles Fitzpatrick, Chief Justice of the Supreme Court of Canada; the Honorable W. H. Hearst, Minister of Lands, Forests and Mines; Acting Mayor Church, of Toronto, and President Falconer, for the University of Toronto.

The committees appointed to study various subjects presented their reports, while general discussions on many important topics were carried on at special meetings, and informal discussions were numerous. The committee reports presented were from:

1. International Glacier Committee.

- 2. Committee of the International Geological Map of Europe.
- 3. Palæontologia Universalis Committee.

4. Spendiarow Prize Committee.

5. Stratigraphical Lexicon Committee.

- 6. Committee on Valuation of Iron Ore Resources.
- 7. Committee on Institute for Study of Volcanoes.

8. Fossil Man Committee.

The principal topics for general discussion were:

1. Coal Resources of the World.

2. Differentiation in Igneous Magmas.

3. The Influence of Depth on the Character of Metalliferous Deposits.

4. The Origin and Extent of the pre-Cambrian Sedimentaries.

5. The Subdivisions, Correlation, and Terminology of the pre-Cambrian.

6. To what Extent was the Ice Age Broken by Interglacial Periods?

7. The Physical and Faunal Characteristics of the Palæozoic Seas with Reference to the Value of the Recurrence of Seas in Establishing Geological Systems.

In addition to the above subjects numerous other topics were introduced and considered during the meeting.

The most elaborately treated subject was the "Coal Resources of the World," on which a monograph had been pre-

pared under the direction of the Canadian members of the Congress. It comprises three quarto volumes and an atlas, and the different parts of it are written by geologists of different countries. The coal resources of over sixty countries are described, most of the papers being in English and all being summarized in English. The publication, in fact, is a compilation of papers on the coal of every section of the world, written by specialists on each field. It is a wonderful work and reflects credit alike on the individual writers and on the Canadian geologists who compiled and edited it. At the last previous meeting of the Geological Congress, which was in Stockholm in 1910, a similar monograph on the "Iron Ore Resources of the World" was gotten up for the occasion and the precedent has now been strongly set for similar monographs on important geological subjects to commemorate future meetings.

The International Geological Congress as an organization is over thirty-five years old and had its origin at the Centennial Exhibition in Philadelphia in 1876, where a collection of maps and other geological records of different parts of the world called the attention of scientists to the desirability of international meetings to facilitate the exchange of ideas and data among the geologists of the world. At a meeting of the American Association for the Advancement of Science in Buffalo, in the summer of the same year, the idea was further elaborated, and a commission was appointed to organize an international geological congress to be held in Paris at the time of the exhibition there in 1878. The plan was carried out, and over twenty different countries were represented by delegates at this first Congress. So successful was it that the Congresses have been held at intervals of about three years ever since and the meetings have taken place in different parts of Europe and America. Over twenty years ago the Congress met in Washington; this year it was held in Canada, at the invitation of the Canadian Government, and the next Congress will be held in Belgium, at the invitation of that country.

The International Geological Congress is governed by a council, but usually the country in which the Congress meets makes what general arrangements it sees fit for conducting the proceedings. At the Toronto meeting, however, steps were taken to formulate an arrangement for a permanent organization to direct the methods and procedures of the meetings wherever held.

About nine hundred members were enrolled in the lists of the Twelfth International Geological Congress, and of this number about four hundred and fifty were actually present. The Canadians and Americans were the most numerous, though there were also many members from Great Britain and Germany, while France, Italy, Russia, Austria, Belgium, and Sweden sent large delegations, and Norway, Argentine Republic, Japan, China, and many other countries were well represented; in fact, delegates from over forty different countries were present, so that the Congress was international in fact as well as in name. The various governments, as well as many of the great universities and scientific societies throughout the world, were represented by delegates.

The management of the Congress by the Canadians was excellent. Everything was done that could add to the comfort, interest, and pleasure of the members. The people of Toronto and of Canada in general were most hospitable and kind, and no member of the Congress could have left Canada without the pleasantest recollections of its people and their boundless hospitality.

New Central Battery Telephone Traffic Distributer. V. J. BAUMANN. (Elektrotechn. Zeitschr., xxxiv, 583.)—In central battery manual telephone exchanges each subscriber has individual calling and cut-off relays with signal lamps. The subscribers are divided into groups, each of which is assigned to an answering or A operator. The calling rate differs not only at various times of the day, but also for different subscribers, and the work thrown on the operators is consequently very unequal. Avén, of Stockholm, has modified the usual arrangement by automatically indicating to the A operator a disengaged B operator, and the adoption of this modification has resulted in a reduction in the size of the multiple by about 50 per cent. The more evenly the work can be distributed among the operating staff, the more efficiently can the apparatus be used and economies in equipment and operating can be effected. The author describes a central battery automatic traffic distributer, in which all incoming calls are equally distributed to the operating staff. The subscribers' equipment is reduced at the exchange, as there is no necessity for calling and cut-off relays or answering jacks, and consequently there are no relay racks required and the I. D. F. is dispensed with. The circuit arrangements are such that no operator receives more than one call at any given instant. The paper should be referred to for a full description of the arrangement with the accompanying diagram.

#### NOTES FROM THE U.S. BUREAU OF STANDARDS.\*

#### THE MELTING-POINTS OF SOME REFRACTORY OXIDES.†

By C. W. Kanolt,

Bureau of Standards.

The oxides were melted in a graphite resistance furnace. The melting-points were determined by means of heating curves, the temperatures being measured with a Morse optical pyrometer of the Holborn-Kurlbaum type.

The pyrometer was calibrated against the melting-points of antimony (630°), copper-silver eutectic (779°), silver (960°), copper (1083°), and diopside (1391°). Absorption glasses were used in measuring temperatures above 1400°. As a check upon the work five determinations of the melting-point of platinum were made in an iridium furnace. The weighted mean was 1755°, with an average deviation of 5°. This is identical with the value accepted by the Bureau of Standards.

The greatest difficulties in work with the oxides are the avoidance of smoke, which would give low temperature readings, and the prevention of the contamination of the oxide by the material

used as a support.

Magnesia was melted in graphite, alumina in graphite and in tungsten, chromium oxide in tungsten, and lime in tungsten. Lime was also made into tubes, which were supported by the upper end in the cooler part of the furnace, while the lower end extended into the hottest part and was melted. The pyrometer was sighted into the tube. When crucibles were used, slender tubes of the same material as the crucible were inserted in the material to be melted and the pyrometer was sighted down these tubes.

Smoke may be avoided by the use of a sufficiently high vacuum, but lime and magnesia could not be melted in a vacuum on account of rapid vaporization. In these cases the furnace was filled with hydrogen or other gas at atmospheric pressure, and the inner tube was kept free from smoke by a gentle current of the gas.

<sup>\*</sup> Communicated by the Bureau.

<sup>†</sup>Shortly to appear as scientific paper reprint from the Bulletin of the Bureau of Standards.

The cooling effect of the gas current was found to be negligible. When a lime tube was used it was freed from smoke in the same way.

The method in which the material to be melted is made into a tube appears to be the most promising one for further use.

The results are summarized in the following table:

Oxide	Melting-point, Centigrade degrees.	. Number of determinations.	Average deviations, degrees.
MgO	2800	6	13
CaO	2572	. 5	3
A1 <sub>2</sub> O <sub>3</sub>	2050	8	4
$Cr_2O_3$	1990	5	6

#### THE PENTANE LAMP AS A WORKING STANDARD.\*

By E. C. Crittenden and A. H. Taylor.

For several years an investigation of various flame standards of candle-power has been in progress at the Bureau of Standards. This investigation has been made with the double purpose of determining whether any of the flame lamps are capable of furnishing a check on a possible drift in the value of the unit now maintained by electric incandescent standards, and of finding a satisfactory working standard for use where electric standards are impracticable.

The results have been distinctly favorable to the use of the Harcourt 10-candle pentane lamp as a secondary standard. This lamp has the disadvantages of being large and not easily portable, of using fuel which is expensive and somewhat dangerous, and of requiring more air than ordinary ventilation will supply. In spite of these faults its use is increasing, chiefly because it appears to be the only standard of candle-power now in use, other than incandescent electric lamps, which can be relied upon to give, under the usual working conditions, the degree of accuracy expected in present commercial practice.

A given lamp will repeat its value very closely, but the normal candle-power is usually not exactly ten, and the exact value must be determined by a photometric test. Since the lamp itself is only an instrument for producing the actual standard, the flame, there is little significance in a value given for the lamp unless other

<sup>\*</sup> To be published in the Bulletin of the Bureau of Standards and in the Transactions of the Illuminating Engineering Society.

factors, such as air and fuel and other conditions of operation, are known. The value certified for a lamp applies strictly only for its use under conditions identical with those under which it was standardized; a large part of the paper is therefore devoted to a description of the method of testing followed at the Bureau of Standards and to general directions for the use of the lamps.

Especial attention is given to the effects of variation in pentane and of atmospheric conditions. It is found that the pentane commercially obtainable increases in density rather rapidly by the fractional distillation which occurs in the lamp. The density (at 15° C.) should be between 0.6235 and 0.626, but it usually reaches 0.635 when a little over half of the liquid has been used. Beyond this point there is a marked increase in the intensity of the flame as the density of the fuel becomes greater. For an approximate correction, which will make possible a considerable economy in fuel without much sacrifice in accuracy, the variation may be assumed to be linear and to be one per cent. in candle-power for each 0.01 in the density of the liquid.

When the lamps are operated in a well-ventilated room the most important cause of variation is humidity. Water vapor in the air lowers the intensity of the flame, the decrease being proportional to the amount of vapor. Since variations due to this cause may exceed 15 per cent., the water vapor correction is very important. Previous work at the Bureau \* has indicated that one per cent. of water vapor in the air causes a decrease of 5.67 per cent. in the candle-power of the pentane flame, whereas the correction officially established in England is 6.6 per cent. The present paper gives further data based on about 75,000 photometer settings on 27 lamps, including all those tested in 1911 and 1912, whose tests have extended over a range of 0.5 per cent. or more of water vapor in the air. The mean result is an exact check of the correction factor previously found at the Bureau.

To facilitate the reduction of observations on flames to normal candle-powers, a chart is given from which the departure of a lamp from normal value can be read directly when the barometric pressure and the readings of the wet and dry bulb thermometers of a ventilated hygrometer are known. The chart is plotted for the pentane lamp, but it may be applied to other flames without introducing serious errors. It would certainly be justifiable to measure

<sup>\*</sup> Rosa and Crittenden, Trans. Illuminating Engineering Society, 5, p. 753 (1910).

gas flames, for instance, with electric standards and to correct the observed candle-powers to obtain normal values according to the chart.

#### PYROMETER TESTING AND HEAT MEASUREMENTS.\*

The object of this circular has been to answer as far as possible the frequent inquiries addressed to the Bureau concerning high temperature measurements, the general use of pyrometers, the regulations governing their acceptance for test, etc., and to briefly discuss various technical points which are of especial importance in this field of work. The following topics are treated:

- 1. Temperature scale.
- 2. Thermoelectric pyrometers.
  - (a) Homogeneity.
  - (b) Annealing.
  - (c) Precautions.
  - (d) Calibration.
  - (e) Temperature of cold junction.
  - (f) Use of a pyrometer galvanometer of low resistance.
  - (g) Temperature coefficient of galvanometer.
- 3. Electrical resistance thermometers.
  - (a) Calibration.
- 4. Optical and radiation pyrometers.
  - (a) Calibration.
- 5. Expansion and other pyrometers.
  - (a) Recording instruments.
- 6. Heat measurements.
- 7. Publications in thermometry, pyrometry, and heat measurements. (Bureau of Standards Bulletin.)
  - 8. Regulations concerning tests.
    - (a) Application for test.
    - (b) Identification marks.
    - (c) Shipping directions.
    - (d) Address.
    - (e) Remittances.
    - (f) Breakage.
  - 9. Fees.

<sup>\*</sup>Circular of the Bureau of Standards No. 7, 5th edition, October 1913, 16 pages.

# THE FRANKLIN INSTITUTE

(Proceedings of the Special Meeting, held Thursday, October 2, 1913.)

HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, October 2, 1913.

In pursuance to the following call:

THE FRANKLIN INSTITUTE, 15 South Seventh Street,

September 27, 1913.

A Special Meeting of the Institute will be held on Thursday, October 2d, at four o'clock P.M., in the Hall of the Institute, to determine whether the site acquired at Sixteenth and Arch Streets for the use of The Franklin Institute has become unsuitable for or unadapted to the purposes of The Franklin Institute, and to pass upon the action of the Board of Managers in acquiring a new site.

R. B. Owens, Secretary.

a special meeting of the Institute was held this afternoon at four o'clock.

PRESIDENT WALTON CLARK in the Chair.

A quorum being present, Mr. Henry Howson, Chairman of the Institute's Franklin Fund and Building Committee, stated that the Board of Managers recommended to the Institute the sale of the Institute's property on the southeast corner of Sixteenth and Arch Streets, it having become unsuitable and unadapted to the purposes of the Institute by reason of the plotting across its surface of the Park Boulevard, and offered the following resolutions, which were unanimously adopted:

"Resolved, That, in the judgment of the members of The Franklin Institute, the plot of ground situate on the southeast corner of Sixteenth and Arch Streets, 44 feet on Arch Street by 150 feet on Sixteenth Street, acquired for the purpose of erecting thereon a building for the use of The Franklin Institute, has, by reason of the plotting across its surface of the Park Boulevard, become unsuitable for and unadapted to the purposes of The Franklin Institute, in carrying out the provisions of the trust created under the agreement of February 4, 1907, with the City of Philadelphia, therein created Trustee.

"Resolved, That the City of Philadelphia, Trustee, is hereby requested and authorized to sell the said lot of ground situate on the southeast corner of Sixteenth and Arch Streets, 44 feet on Arch Street by 150 feet on Sixteenth Street, for such price and upon such terms as may to it seem right and proper, and that the purchaser under such sale shall take title, without

any responsibility concerning the application of the purchase money or other consideration; we hereby consenting to such sale, and to the application of the proceeds thereof in the purchase by the said City of Philadelphia, Trustee, of other premises and the erection thereon of another building or buildings for the purposes and upon the trusts prescribed in the said agreement of February 4, 1907.

"Resolved, That the proper officers be, and they are hereby, authorized to certify to the passage of the above resolution and to attach the seal of the

Institute thereto.

"Resolved, That the President of The Franklin Institute be authorized, on behalf of said Institute, to join with the City of Philadelphia, Trustee, in a petition to the Court of Common Pleas of Philadelphia County, setting forth the fact that the plot of ground situate on the southeast corner of Sixteenth and Arch Streets, 44 feet on Arch Street by 150 feet on Sixteenth Street, acquired for the purpose of erecting thereon a building for the use of The Franklin Institute, has, by reason of the plotting across its surface of the Park Boulevard, become unsuitable for and unadapted to the purposes of The Franklin Institute, in carrying out the provisions of the trust created under the agreement of February 4, 1907, with the City of Philadelphia, therein created Trustee, and asking the consent of the said Court to the sale of said property for such a price and upon such terms as may be fixed by the City of Philadelphia, Trustee, and to the application of the proceeds thereof in the purchase by the said City of Philadelphia, Trustee, of other premises and the erection thereon of another building or buildings for the purposes and upon the trusts prescribed in the said agreement of February 4, 1907."

Mr. Howson then stated that the Board of Managers had obtained options on the following properties between Race and Cherry Streets: 1826, 1828, 1830, 1832, and 1834 Race Street; 133, 137, 139, and 141 North Nineteenth Street, and asked the Institute's approval of this choice by the Board of Managers of a site for a new building.

On motion, duly seconded, it was resolved that the action of the Board of Managers in securing options on the above properties be approved and that the Board of Managers be requested to complete the purchase.

R. B. Owens, Secretary.

(Proceedings of the Stated Meeting held Wednesday, October 15, 1913.)

HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, October 15, 1913.

VICE-PRESIDENT JAMES M. DODGE in the Chair.

Additions to membership since last report, 105.

The following proposed amendment to the By-laws, presented at the May meeting, was submitted for final action:

Article iv, Section 1, of the By-laws to be amended by striking out everything after "January" in the third line, and substituting the following words:

"March in each year shall pay, in advance, for the current year, one-half of the annual dues," so that the section as amended will read:

"The annual payment of fees for membership shall be due and payable on the first of October in each year, in advance; but all members elected after the 31st of March in each year, shall pay, in advance, for the current year, one-half of the annual dues."

On motion, duly seconded, the amendment was adopted.

The Chairman then introduced Mr. Emile Berliner, of Washington, D. C., who presented a communication on "The Revolving Cylinder Internal Combustion Motor."

Revolving cylinder motors present mechanical problems and mechanical movements differing from those of reciprocating motors and from turbines, and they are a class in themselves, taking a position between the two others. The mechanism is non-reciprocating, but the gas action is, and this fact enables them to give as much power as reciprocating motors, but with the smoothness of running of a turbine. Centrifugal force is the most important factor to be dealt with and furnishes problems of great difficulty. The subject was illustrated by working models and diagrams.

A discussion followed the reading of the paper, and the following gentlemen participated: Messrs. Henderson, Levy, Bilgram, Morris, Stratton, Crisfield: Professors Fernald and Barnes, and others.

On motion, duly seconded, the thanks of the meeting were extended to the speaker and the paper was referred for publication.

Adjourned.

R. B. Owens, Secretary.

#### COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, October 1, 1913.)

> HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, PA., October 1, 1913.

DR. GEORGE A. HOADLEY in the Chair.

The following report was presented for final action:

No. 2522.—Gaede's Molecular Air-Pump. Elliott Cresson Medal. Adopted.

The following reports were presented for first reading:

No. 2527.-Norton "Alundum."

No. 2535.—Tirrill Voltage Regulator.

No. 2543.—Kinkead Shaft-Levelling Device.

R. B. OWENS, Secretary.

## SECTIONS.

A meeting of the Electrical Section was held in the Hall of the Institute on Thursday evening, October 2, 1913, at 8 o'clock.

Mr. W. C. L. Eglin, President, occupied the chair.

The minutes of the previous meeting were approved as published.

Dr. Chas. P. Steinmetz, Consulting Engineer, General Electric Company, and Professor of Electrical Engineering, Union College, Schenectady, N. Y., presented a paper entitled "The Effect of Electrical Engineering on Modern Industry."

The speaker considered the economy of the present methods of industrial production of electrical energy and outlined the adjustments of operating conditions necessary to increase this economy.

After some discussion, the thanks of the meeting were extended the speaker.

Adjourned.

R. B. Owens, Secretary.

## MEMBERSHIP NOTES.

## Elections to Membership.

(Stated Meeting of the Board of Managers, October 8, 1913.)

#### RESIDENT.

MR. FRANCIS X. DAILY, 1521 North Seventeenth Street, Philadelphia, Pa.

#### NON-RESIDENT.

MR. LUTHER D. BURLINGAME, 15 Catalpa Road, Providence, R. I.

MR. RALPH E. FLANDERS, Jones & Lamson Machine Company, Springfield, Vt.

Mr. George A. Orrok, 232 East Seventeenth Street, Flatbush, N. Y.

MR. JOHN RIDDELL, General Electric Company, Schenectady, N. Y.

#### ASSOCIATE.

MR. JOHN MCALLISTER, Gibbsboro, N. J.

#### Changes of Address.

Mr. W. S. Atkinson, 90 Bartley Avenue, Mansfield, Ohio.

MR. HAROLD V. COES, 982 Beacon Street, Newton Centre, Mass.

MISS EMILY E. Howson, 222 Langdon Street, Madison, Wis.

Prof. G. Lanza, The Montevista, Sixty-third and Oxford Streets, Philadelphia, Pa.

MR. NORMAN MACBETH, 246 West End Avenue, New York City, N. Y.

MR. Donald McDonald, Louisville Gas and Electric Company, 311 West Chestnut Street, Louisville, Ky.

MR. LOUIS M. PAWLETT, 771 Myrtle Avenue, Bridgeport, Conn.

LIEUT.-Col. Samuel Reber, Signal Office, War Department, Washington, D. C.

MR. FREDERICK W. SALMON, 719 Eighteenth Street, Birmingham, Ala.

MR. RICHARD SELLERS, Bellevue, Del.

Mrs. William Sellers, Bellevue, Del.

MR. ELMER A. SPERRY, The Sperry Gyroscope Company, 126 Nassau Street, Brooklyn, N. Y.

Mr. G. Von Utassy, 119 West Fortieth Street, New York City.

Mr. Robert W. Withington, The American Insulating Machine Company, corner Fairhill and Huntingdon Streets, Philadelphia, Pa.

Mr. H. S. Worrell, 36 East Montgomery Avenue, Philadelphia, Pa.

## LIBRARY NOTES.

#### Purchases.

American Electrochemical Society Transactions, vol. 23. 1913.

Сони, G.—Die Pyrazolfarbstoffe. 1910.

COLVIN, F. H., and F. A. STANLEY.—American Machinist Grinding Book. 1912. GREENE, A. M., JR.—The Elements of Heating and Ventilation, 1st edition. 1913.

HELDT, P. M.—The Gasoline Automobile, vol. 2. 1913.

International Geological Congress, XII, Canada.—The Coal Resources of the World. 4 vols. 1913.

LORD, N. W., and D. J. Demorest.—Metallurgical Analysis, 3d edition. 1913. MARTIN, G.—Industrial and Manufacturing Chemistry Organic. 1913.

RYAN, W. T.—Design of Electrical Machinery. 3 volumes, 1st edition. 1912. SCHULTZ, G.—Farbstofftabellen. 1911–1913.

Soddy, F.—The Interpretation of Radium. 3d edition. 1912.

#### Gifts.

American Institute of Metals, Transactions, vol. 6. Buffalo, 1913. (From the Institute.)

American Society for Testing Materials, Year-Book 1913. No place, 1913. (From the Society.)

Associations des Ingénieurs Sortis des Cinq Écoles Belges, Annuaire général des ingénieurs diplômés en Belgique, 2d edition, 1912. Gand, Belgium, no date. (From the Association.)

Baldwin Locomotive Works, Forty Thousandth Locomotive. Philadelphia, 1913. (From the Works.)

Baltimore Department of Health, Annual Report, 1912. Baltimore, 1912. (From the Department.)

Boston and Maine Railroad, 80th Annual Report, 1913. Boston, 1913. (From the Railroad.)

Canada Department of Mines: Economic Minerals and Mining Industries of Canada. Ottawa, 1913. (From the Department.)

Canada Department of Mines: Memoir 33, The Geology of Gowanda Mining Division, by W. H. Collins. Ottawa, 1913. (From the Department.)

Canadian Mining Institute, Index of the Journal, vols. 1-10, 1898-1907. Montreal, 1913. (From the Institute.) Canadian Pacific Railway Company, Report of the 32d Annual Meeting. Montreal, 1913. (From the Company.)

Canadian Society of Civil Engineers, Transactions, vol. 26, part 2. Montreal, 1913. (From the Society.)

Chicago & North-Western Railway Company, 54th Annual Report, June 30, 1913. Chicago, 1913. (From Mr. R. D. Jenks.)

Chicago, Rock Island & Pacific Railway Company, 33d Annual Report, June 30, 1913. Chicago, 1913. (From the Company.)

Denver & Rio Grande Railroad Company, 27th Annual Report, 1913. No place, no date. (From the General Auditor.)

Detroit Twist Drill Company, Catalogue No. 16 and Form No. 18, Drills. Detroit, no date. (From the Company.)

Drexel Institute, Year-Book 1913-1914. Philadelphia, 1913. (From the Institute.)

Engineers' Club of Philadelphia, Directory 1913. Philadelphia, 1913. (From the Club.)

Gold Car Heating and Lighting Company, Catalogue 1910, Gold Systems of Heating and Lighting of Railway Cars. New York, no date. (From the Company.)

Great Britain Meteorological Committee, Eighth Annual Report, 1913. London, 1913. (From the Meteorological Department.)

Jefferson Physical Laboratory of Harvard University, Contributions, vol. 10, 1912. Cambridge, Mass., 1913. (From the Laboratory.)

K. Vitterhets Historie och Antikvitets Akademien, Fornvännen, 1912. Stockholm, Sweden, no date. (From the Akademien.)

Lake Mohonk Conference on International Arbitration, 19th Report, May, 1913. Mohonk Lake, 1913. (From the Secretary.)

Lewis Institute, Annual Register, 1912-1913. Chicago, 1913. (From the Institute.)

Maryland Geological Survey, Devonian, 3 volumes. Baltimore, 1913. (From the State Geologist.)

Mason Regulator Company, Catalogue No. 66, Pressure Regulating Devices. Boston, 1913. (From the Company.)

Massachusetts Board of Gas and Electric Light Commissioners' 28th Annual Report, 1912. Boston, 1913. (From the Board.)

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation Bulletin No. 4, The Economic Cost of the Smoke Nuisance to Pittsburgh, by John J. O'Connor, Jr. Pittsburgh, 1913. (From the Institute.)

Minneapolis, St. Paul & Sault Ste. Marie Railway Company, 25th Annual Report. Minneapolis, 1913. (From the Company.)

Minnesota Railroad and Warehouse Commission, 28th Annual Report, 1912. Minneapolis, 1913. (From the Commission.)

New South Wales Department of Mines: Mineral Resources No. 7, Mercury or Quicksilver in New South Wales, by J. E. Crane. Sydney, 1913. (From the Minister for Mines.)

Newton City Engineer, Annual Report, 1912. Newton, Mass., 1913. (From the City Engineer.)

- New York, Ontario & Western Railway Company, 34th Annual Report. New York City, 1913. (From the Company.)
- New York State Public Service Commission for the First District, Report for 1911, vol. 3. New York, no date. (From the Commission.)
- New York State Public Service Commission for the Second District, Sixth Annual Report, 1912, 2 volumes. Albany, 1913. (From the Commission.)
- Ohio Chief Inspector of Mines, 38th Annual Report, 1912. Springfield, 1913. (From the Inspector.)
- Ohio Northern University, Catalogue 1913-1914 and Calendar 1913-1914 of the College of Engineering. Ada, 1913. (From the University.)
- Ohio State University, Catalogue May, 1913. Columbus, 1913. (From the University.)
- Ontario Bureau of Mines: Report vol. 19, part 2, The Cobalt-Nickel Arsenides and Silver Deposits of Temiskaming, by W. G. Miller. Toronto, 1913. (From the Bureau.)
- Ontario Entomological Society, 43d Annual Report. Ontario Fruit Growers' Association, 44th Annual Report. Toronto, 1913. (From the Ontario Department of Agriculture.)
- Osaka Imperial Mint, Report of the Director, 1913. Osaka, Japan, 1913. (From the Director.)
- Patents, Copyrights and Trade-Marks, by W. Henry Elfreth. New York, 1913. (From the Author.)
- Philadelphia Museums, Annual Report 1912. Philadelphia, 1913. (From the Museums.)
- Philadelphia Transit Commissioner, Report July, 1913, vols. 1 and 2. Philadelphia, no date. (From the Director of the City Transit.)
- The Railway Library, 1912, edited by Slason Thompson. Chicago, 1913. (From the Editor.)
- Royal Society of Canada, Proceedings and Transactions, 3d series, vol. 6, 1913. Ottawa, 1913. (From the Honorable Secretary.)
- St. Louis Water Commissioner, Annual Report April, 1913. St. Louis, 1913. (From the Commissioner.)
- Staffordshire Iron and Steel Institute, Proceedings, vol. 28, 1912–1913. Stourbridge, England, 1913. (From the Institute.)
- L. S. Starrett Company, Catalogue No. 20, Fine Mechanical Tools. Athol, Mass., no date. (From the Company.)
- Statistisches Taschenbuch für das Deutsche Reich. von Erich Simon, 4th Jahrgang, 1913. Berlin, 1913. (From Mr. R. D. Jenks.)
- Tasmania Department of Mines: Geological Survey Bulletin No. 13, The Preolenna Coal Field and the Geology of the Wynyard District, by Loftus Hills. Hobart, 1913. (From the Department.)
- Tasmania Secretary for Mines, Report 1912. Hobart, 1913. (From the Secretary.)
- Technische Hochschule zu Karlsruhe, 25 publications issued during the school year 1912–1913. Karlsruhe, Germany, 1912–1913. (From the Hochschule.)
- Triumph Ice Machine Company, Catalogue E, Triumph Ammonia Fittings. Cincinnati, 1913. (From the Company.)
  - Vol. CLXXVI, No. 1055-42

University of Pennsylvania, Catalogue 1912-1913. Philadelphia, 1913. (From the University.)

Victoria Mines Department, Annual Report of the Secretary for Mines, 1912. Melbourne, 1913. (From the Secretary.)

Western Australia Statistical Register, 1911. Perth, 1913. (From the Registrar General.)

Wisconsin Geological and Natural History Survey Bulletin No. 26, The Geography and Industries of Wisconsin, by Ray Hughes Whitbeck. Madison, 1913. (From the Survey.)

Wisconsin State Historical Society, Collections, vol. 20. Madison, 1911.

(From the Society.)

Henry R. Worthington Pump Company, "Irrigation": Conservation and Distribution of Water for Irrigation. New York, no date. (From the Company.)

Yale University, Report of the Treasurer, 1912-1913. New Haven, 1913.

(From the University.)

## BOOK NOTICES.

U. S. DEPARTMENT OF AGRICULTURE.—Bureau of Plant Industry, Bulletin No 285: "The Water Requirement of Plants," a review of the literature, by Lyman J. Briggs, Biophysicist in Charge of Biophysical Investigations, and H. L. Shantz, Plant Physiologist. 96 pages, illustrations, 8vo. Washington, Government Printing Office, 1913.

This review of the literature on the water requirement of plants supplies an extended bibliography of the subject and presents the results of the leading experiments.

Among the topics considered are the effect of soil moisture content, soil type, cultivation, soil mass, fertilizers, previous crops, soil temperatures, air temperatures, shade, air, humidity, carbon dioxide content of the air, parasites, the relative leaf area, frequent cutting, defoliation, amount of growth or number of plants per unit of soil mass, and the bearing of the age of the plant on its water requirement.

In addition, there is a consideration of the water requirement of different kinds of plants, and the determination of water requirement of crops under field conditions.

JOURNAL OF AGRICULTURAL RESEARCH,—The first number of the new Journal of Agricultural Research published by the U. S. Department of Agriculture was issued October 10th. It consists of eighty-seven pages of letter-press and line drawings and five plates, including one color plate. The articles in the first number are:

Citrus Ichangensis, a Promising, Hardy, New Species from Southwestern China and Assam.

Cysticercus Ovis, the Cause of Tapeworm Cysts in Mutton.

The Serpentine Leaf-Miner.

The introduction is written by Dr. B. T. Galloway, Assistant Secretary, and outlines the purposes of the journal.

The first few issues will contain papers from the Department of Agriculture only. The later numbers, however, will probably include articles prepared and submitted by investigators in the State agricultural colleges and experiment stations. The book is highly technical in character and will not be circulated except among scientific specialists.

## PUBLICATIONS RECEIVED.

Electrical and Magnetic Calculations for the Use of Electrical Engineers and Artisans, Teachers, Students and all others Interested in the Theory and Application of Electricity and Magnetism, by A. A. Atkinson, M.S., Professor of Physics and Electrical Engineering in Ohio University, Athens, Ohio. Fourth edition. 310 pages, illustrations, plates, 12mo. New York, D. Van Nostrand Company, 1913. Price, \$1.50.

Physical Measurements, by A. Wilmer Duff, Professor of Physics in the Worcester Polytechnic Institute, and Arthur W. Ewell, Professor of Physics in the Worcester Polytechnic Institute. Third edition, revised and enlarged. 244 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son & Co., 1913. Price, \$1.50.

A New Era in Chemistry. Some of the Most Important Developments in General Chemistry during the last Quarter of a Century, by Harry C. Jones. 326 pages, 12mo. New York, D. Van Nostrand Company, 1913. Price, \$2.

The Gyroscope, by F. J. B. Cordeiro. 105 pages, illustrations, 12mo. New

York, Spon & Chamberlain, 1913. Price, \$1.50.

Canada Department of Mines: Economic Minerals and Mining Industries of Canada, by the Staff of the Mines Branch. 77 pages, illustrations, map, 8vo. Ottawa, Government Printing Bureau, 1913.

Business Methods in Municipal Works. An Informal Record of the Operations of the Department of Public Works of the City of Philadelphia under the Administration of Mayor Blankenburg. 64 pages, 8vo. Philadelphia, Department of Public Works, 1913.

A Nation's Neglect, by Marcus A. Dow, General Safety Agent, New York Central Lines. Reprinted from the Outlook, issue of September 27, 1913. 10 pages, illustrations, 8vo. New York, Kempster Printing Company, 1913.

Diagram Giving Stresses in Beams, by H. R. Thayer, Assistant Professor of Structural Design, Carnegie Institute of Technology. Sheet 9 × 12 inches. New York, D. Van Nostrand Company, 1910. Price, 20 cents.

Seventh Annual Convention Illuminating Engineering Society, Souvenir Program. 40 pages, illustrations, 12mo. Pittsburgh, Pa., issued by General Convention Committee, 1913.

U. S. Bureau of Mines: Bulletin 22, Analyses of Coal in the United States, with description of mine and field samples collected between July 1, 1904, and June 30, 1910, by N. W. Lord, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford. Part I—Analyses; Part II—Descriptions of Samples. 2 volumes, 8vo. Bulletin 64, The Titaniferous Iron Ores in the United States: Their Composition and Economic Value, by Joseph T. Singewald, Jr. 145 pages, illustrations, plates. 8vo. Technical Paper 33, Sanitation at Mining Villages in the Birmingham District, Alabama, by Dwight

E. Woodbridge. 26 pages, illustrations, map, 8vo. Technical Paper 43, The Influence of Inert Gases on Inflammable Gaseous Mixtures, by J. K. Clement. 24 pages, illustrations, plates, 8vo. Monthly Statement of Coal-Mine Fatalities in the United States, July, 1913, with revised figures for preceding months, compiled by Albert H. Fay. 19 pages, 8vo. Washington, Government Printing Office, 1913.

The Cost to the United States and its Cotton Producers of the Clarke Amendment to the Tariff Act Imposing a Prohibitive Tax on Contracts for the Future Delivery of Cotton made upon Cotton Exchanges, by Arthur Richmond Marsh. 15 pages, 8vo. New York, 1913.

U. S. Department of Commerce and Labor: Circular of the Bureau of Standards, S. W. Stratton, Director. No. 42, Metallographic Testing. 16

pages, 8vo. Washington, Government Printing Office, 1913.

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation.—Bulletin No. 4, The Economic Cost of the Smoke Nuisance to Pittsburgh, by John J. O'Connor, Jr., A.B. 46 pages, 8vo. Pittsburgh, Pa., University of Pittsburgh, 1913.

Canada Department of Mines: A General Summary of the Mineral Production of Canada during the Calendar Year 1912, by John McLeish, B.A., Chief of the Division of Mineral Resources and Statistics. 46 pages, 8vo. Ottawa, Government Printing Bureau, 1913.

U. S. Department of Agriculture: Bulletin No. 12, Uses of Commercial Woods of the United States, by H. W. Maxwell, Expert. 54 pages, 8vo. Bulletin No. 23, Vitrified Brick as a Paving Material for Country Roads, by Vernon M. Peirce, Chief Engineer, and Charles H. Moorefield, Senior Highway Officer, Office of Public Roads. 34 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1913.

South Philadelphia: The Abolishment of Grade Crossings and the Creation of Opportunities for Commercial and Industrial Development. 72 pages, illustrations, plates, tables, 8vo. Philadelphia, Department of Public Works, 1913.

The Registration of Vital Statistics and Good Business, an address delivered before the Annual Conference of Health Officers of the State of Indiana, Indianapolis, May 13, 1913, by Louis I. Dublin, Ph.D., Statistician Metropolitan Life Insurance Company. 16 pages, illustrations, 8vo. New York, 1913.

Ontario Bureau of Mines: Report vol. xix, part ii, The Cobalt-Nickel Arsenides and Silver Deposits of Temiskaming (cobalt and adjacent areas). by Willet G. Miller, Provincial Geologist. Fourth edition. 279 pages, illustrations, plates, maps, 8vo. Toronto, King's Printer, 1913.

Railway Routes in Alaska: Message from the President of the United States Transmitting Maps and Profiles to Accompany the Report of the Alaska Railroad Commission. 19 plates, maps, profiles, 8vo. Washington, Government Printing Office, 1913.

U. S. Department of Commerce: Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory near Honolulu, Hawaii, 1911 and 1912, by Daniel L. Hazard, Computer, Division of Terrestrial Magnetism. 99 pages, plates, quarto. Washington, Government Printing Office, 1913.

# **CURRENT TOPICS**

Artificial Caoutchouc from the Scientific Aspect. C. HARRIES. (Chem. Zcit., xxxvi, 654.)—Emphasis is laid on the ozone method of investigating the structure and composition of synthetic caoutchoucs. This method has proved the chemical identity of synthetic isoprene caoutchouc with the natural product. The ozonide of sodium-isoprene caoutchouc, on the other hand, gives a different scission curve and different decomposition products, therefore its chemical nature must be entirely different. The so-called piperylene caoutchouc, obtained by heating  $\alpha$ -methylbutadiene, contrary to expectation, proved to be different from isoprene caoutchouc, while gutta-percha resembles it closely, though very different externally. The study of the ozonide has proved that the doubly unsaturated  $\delta$ -ring lies at the basis of the normal rubbers, isoprene caoutchouc having the formula

$$\left(\text{CH}_3 - \text{C} \xrightarrow{\text{CH} - \text{CH}_2 - \text{CH}_2} \text{C} - \text{CH}_3\right) X$$

is still unknown. In the case of butadiene caoutchouc, theory is proved by fact, because its ozonide is identical with that obtained from Willstaetter's 1.5-cyclo-octadiene and gives the same quantity of succinic dialdehyde on decomposition with water. This explains why rubber and gutta-percha give the same ozonide. They are both polymers of the same hydrocarbon, and the difference lies only in the molecular weight.

Dried Bagasse as Fuel. Anon. (Engineering, xciii, 727.)—One pound of undried bagasse with 53.5 per cent. water evaporates 1.63 pounds water, while with dried fuel, having 45.4 per cent. water, there is evaporated 2.53 pounds water from and at 100° C.

Tungsten Daylight Lamp. Anon. (Electrical World, 1xi, 1181.)—In most artificial illuminants, including the tungsten lamp, there is an excess of the red end of the spectrum as compared with daylight. This is illustrated by a diagram. Siemens and Halske have introduced a special screen which, when used with a tungsten lamp, gives progressively increasing absorption in the spectrum between 0.48  $\mu$  and 0.62  $\mu$ . This gives a light approximating in color to daylight for practical purposes, although not exactly equivalent. The lamp is available for voltages from 100 to 130 and 200 to 250. The candle-power is from 70 to 75, and the specific consumption about 1.4 watts per candle-power.

Pinch Effect Electric Furnace. Anon. (Eng., xcv, 2477, 848.) —Dr. Carl Hering, of Philadelphia, demonstrated his process at the Northampton Institute at a meeting of the Faraday Society. The furnace was a small model, and lead was the metal used. Dr. Hering stated that several large furnaces were under construction, one being a three-ton steel furnace. Explaining the principle of his pinch effect, Dr. Hering referred to his well-known type of T-shape furnace, consisting of a vertical tube which opens out at the top to a circular basin. The electrode—a block of steel or of the respective metal—forms the bottom of this tube; above it is the metal, which rises along the axis of the tube at such a speed that a sort of fountain of fused metal is produced. According to Dr. Hering, a jet of liquid metal, through which a very strong electric current is passed, is crushed by electro-magnetic forces, which tends to squeeze the metal out, or up in this case; others explain the effect by the mutual attraction of the parallel lines of force. Dr. Hering further assumes a force which tends to stretch the conductor. In any case the heat developed by intense currents in a restricted conductor is very high, a brisk circulation is set up, and impurities of the metal are carried up to the surface and stay there. As a rule, two parallel resisters or tubes are provided, with an electrode at the bottom of each; on three-phase circuits three resisters are provided. The tubes may be horizontal or inclined. The small furnace shown consisted of an iron pan, mounted in bricks; one half of the pan served as crucible, the other half was taken up by a cubical block of magnesite provided with two parallel horizontal bores, about half an inch in diameter. At the one side the passages ended in vertical openings in the magnesite, through which the electrodes and electrode leads were inserted, and led on the other side to the bath. It could be seen that the metal rushed through both the passages into the molten bath; the motion stopped at once when the current was cut off, and set in again immediately on re-establishing the circuit. The electrodes were joined to the secondary of a transformer, and in actual practice the transformer is made to tilt with the furnace, if that is desirable. Dr. Hering expressed no preference for horizontal or inclined resisters, but remarked that in tilting furnaces the inclination could be altered at will. The resisters suffered less from mechanical erosion than was generally assumed, and the passages could easily be repaired; rammed-down magnesite was mostly used. The furnaces might be provided with several crucibles joined in parallel. They were recommended for steel refining, melting alloys, annealing, and ore smelting. In the latter case a start was made with the metal (e.g., zinc), and a charge of ore and flux was added at the top. As the furnace was quite unobstructed above, although it might be covered, it was convenient for working in rarefied or compressed atmospheres of oxidizing or reducing character. sulphur of a bad iron had been reduced to 0.006 per cent. in one melt. A counter electromotive force was set up in the hot metal, which was an advantage, since it was all converted into heat.

Cumberland's Electrical Process for the Protection of Boilers. (Eng., xcv, 2477, 849.)—This process has been introduced into the United States with the view of preventing corrosion in boilers. It consists of the use of one or more electrodes installed in the boiler, and connected to the positive terminal of a direct-current supply, the boiler being connected to the negative terminal, and the water forms the electrolyte. It is stated that only enough voltage is required to overcome the resistance through the water, and any counter electromotive force due to the difference of potential of the metals of the boiler. A report issued by the United States Navy Department states that some experiments were carried out on a small fire-tube boiler having brass tubes, with a steel shell, in which five polished steel plates were placed: One on the crown sheet, one across the top row of brass tubes, one across the tubes about the middle of the nest of tubes, one on the bottom of the shell-plate under the furnace, and one at the smoke-pipe end. The boiler was filled with water, steam was raised to 190 pounds pressure per square inch, which was kept up for five days, after which the boiler was examined. There were no signs of hydrogen gas, and the electrode placed in the boiler was found to be considerably corroded. The brass tubes showed no corrosion, nor was there corrosion on the test pieces. Underneath the cathode and on the tubes and shell a deposit of black iron dust was found, which was easily washed off. Old scale had also been cracked off the crown sheet and shell in places. The scale on the brass tubes also was cracked off in places and could be easily washed away. The iron electrode in the water was very badly corroded.

Illumination of Interiors. P. S. Millar. (Amer. Illum. Engin. Soc. Trans., viii, 99.)—After some preliminary remarks on the objects of illuminating engineering, the author describes some experiments with small model interiors, each 4 feet long, 4 feet wide, and 3½ feet high. These were used to illustrate the effect of various forms of reflectors, direct and indirect lighting, correct and incorrect positions of lamps, etc. The absorption of various globes is given as follows: Frosted, 6 per cent.; light opal, 13 per cent.; dense opal, 22 per cent. The horizontal illumination with indirect light from ceilings of varied reflecting powers is stated to be (taking a white ceiling as 100): Light cream, 87 per cent.; dark cream, 58 per cent. The illumination derived from direct, semi-indirect, and indirect lighting, with a given expenditure of energy, was found to be: Direct, 1.61 candle-feet; semi-indirect, 1.33 candle-feet; indirect, 0.91 candle-feet.

Slow Ions in Liquid Dielectrics. H. J. VAN DER BIJL. (Deutsch. Phys. Gesell. Verh., xv, 4, 102.)—A discussion on the formulæ for the motion of ions in very viscous media, with special reference to ions produced by radium rays and by ultra-violet light, in vaseline and in aniline.

Osmium-Platinum: a New Alloy. F. ZIMMERMANN. World, ix, 9, 314.)—Of the several metals of the platinum group, platinum, palladium, iridium, and rhodium have been generally used in the industrial arts, either alone or in combination as bivalent Iridium-platinum is the best known, but the increasing scarcity of iridium has led to the search for other combinations of the metals of this group, yielding alloys possessing physical and chemical properties of equal, if not greater, value. The rarer metals of the platinum group are not easily obtained in great purity, and for this reason but little success has been obtained when combined as bivalent alloys. The strong affinity of osmium for oxygen has increased the difficulty of alloying it with other metals in definite proportions. After many experiments the author has successfully combined highly-refined platinum and osmium in widely varying proportions, yielding alloys of commercial value. The two metals may be alloyed in almost any proportions, yet alloys containing from I to Io per cent. osmium and 99 to 90 per cent. platinum are chiefly used. Great purity of the components is essential, as small percentages of other elements appear to be very detrimental to the properties of the resulting alloy. According to the chemical and physical behavior, it seems that one part of osmium in an alloy with platinum will take the place of two and one-half times its weight of iridium. The osmium-platinum alloy is very acid-resisting; and its electrical resistance is considerably higher than that of a similar iridium-platinum alloy. It possesses great hardness and tensile strength, and wires of the finest sizes are drawn with comparative ease.

Power Matters in Textile Mills. F. W. DEAN. (Eng., xcv., 2477, 842.)—A paper read before the National Association of Cotton Manufacturers, Boston, Mass. The question is reviewed under its various aspects. Speaking generally, electricity has so many advantages that probably it will be universally resorted to for power in driving textile mills. It permitted a central steam plant to be used under all circumstances; this added to efficiency and led to minimum charges of all kinds, especially in an "overgrown" mill now having several steam plants. The prime movers in the near future would be steam-turbines operated by superheated steam at a relatively high pressure. He was a strong advocate of fire-tube boilers; they were more economical, more easily cleaned and safer than water-tube boilers. In regard to the purchase of power from outside central stations, he had investigated the point, and had invariably found that it was advantageous for mills to produce their own power rather than to purchase power from an outside source; this was still more particularly the case for mills where a considerable amount of steam was used, and especially where exhaust steam could be utilized for dyeing, starting, heating, etc.

Deterioration of Fire-brick. G. Rigg. (J. Ind. Eng. Chem., v, 549.)—A discussion on the causes of the deterioration of fire-bricks during use, and the conclusion is reached that, other things being equal, the resistance to the action of corrosive slags and gases is greater the more compact and close-textured the brick is. "Spalling" of close-textured brick is due to the use of unsuitable clay, or poor workmanship, or both. It is possible to prepare close-textured fire-brick containing considerable amounts of coarse material, provided that sufficient care be taken in sizing the "grog," so that the interstices between the larger fragments shall be filled as completely as possible by smaller fragments.

Protection of Iron Pipe. Anon. (Amer. Mach., xxxix, 4, 142.) —Iron pipe can be protected from corrosion by heating in a muffle to 1000° F. and admitting steam at the same temperature. This forms a layer of magnetic iron oxide. Smith's process, however, gives better protection. The well-cleaned pipe heated to 700° F. is dipped into a mixture of pitch, coal-tar, and a little linseed oil, which is heated to 300° F. After a few minutes the pipe is drained vertically and cooled. The rapid oxidation of the linseed oil forms a tough binder, as in paint drying.

Absorption of Gas by the Electrodes in the Neon Tube. G. CLAUDE. (Comptes Rendus, clvi, 1317.)—It has been noticed that the electrodes in the neon tube do not readily absorb the gas. It has been found that if the tube is filled with a mixture of one per cent. helium in neon the helium gradually disappears; nitrogen is also absorbed much more readily than neon. In general, the spectrum of a tube containing other gases as impurities gradually changes, until only the neon spectrum remains. This characteristic is fortunate, as it means that a badly-filled tube tends to improve in use.

Utah Metal Production. Anon. (Met. and Chem. Eng., xi, 8, 438.)—According to the U. S. Geological Survey, the total value of gold, silver, copper, lead, and zinc produced in Utah in 1912 was \$42,922,302. There was a decrease of 10 per cent. in the value of gold produced compared with 1911; an increase of 10 per cent. in quantity of silver; a decrease in copper; an increase in lead, and about the same production in zinc. The total production showed an increase in value of about \$6,000,000.

American Agricultural Machinery. Anon. (Eng., xcv, 2477, 857.)—The exports of agricultural machinery from the United States in 1911 reached a value of \$36,241,000. This total was made up as follows: To Russia, \$14,164,000; Argentina, \$13,692,000; Canada, \$8,284,000; Germany, \$4,046,000; Austria-Hungary, \$3,400,000; Australia, \$2,945,000; and Great Britain, \$2,687,000.

Interference Phenomena with Rontgen Rays. W. FRIEDRICH. P. KNIPPING, and M. LAUE. (K. Bayer. Akad. München. Ber., 303.)—According to the generally-accepted theory, the atoms in crystals are arranged in a regular manner as regards spacing throughout the whole crystal. Therefore, if X-rays fall on a crystal, interference effects ought to be observed if the X-rays are similar to light-waves of very short wave-length. In the experiments described a narrow pencil of X-rays fell on a crystal having a photographic plate placed behind it and normal to the beam. Exposures of many hours were made, and on development it was found that, in addition to the central image caused by the main beam, regularlyarranged spots were present on the plate. With powdered coppersulphate, for example, no such effects were observed. The effects were found with crystals of copper sulphate, rock-salt, diamond, and zinc blende. With the plate of the latter (a cubic crystal)  $1.0 \times 1.0 \times 0.05$ cm., cut parallel to one of its principal axes, an extended series of photographs was made with the crystal orientated at different angles. A theoretical examination of the position of the spots in the various photographs is given by M. Laue, the crystal being treated as a three dimensional diffraction grating and the spots as due to the reinforcement of the waves in different directions. The calculated positions of the spots are in good agreement with theory, it being also assumed that definite wave-lengths are present, presumably corresponding to the characteristic X-radiations from the zinc and the sulphur. Five definite wave-lengths are given, varying between 1.27 and  $4.83 \times 10^{-9}$  cm.

The Corrosion of Bronze Propellers. W. Ramsay. (Engineering, xciii, 687.)—The remarkable corrosion of bronze propeller blades used with steam turbines is probably the result of electrolytic action. That part of the blade which is exposed to great strain becomes the anode, while the normal part becomes the cathode, and in the salt water, as an electrolyte, a current flows between them. The hardened or strained metal is attacked or dissolved, while the unstrained metal is comparatively unaffected. The weight of the propeller blades has been reduced too much, they should be stiffened enough to prevent flexure.

The "Oriona" Lamp. De Kermond. (Électricien, xlv, 357.) — This form of lamp consists of a series of tungsten filaments mounted in a horizontal plane in order to improve the illumination immediately under the lamp. It is also possible to make the same arrangement in a vertical plane, or to use a combination of the two methods, so as to obtain the particular distribution of light that circumstances demand. Polar curves contrasting the distribution of light with that from an ordinary tungsten lamp are given. It appears there is an actual gain in the total light emitted, as well as an improvement in the lower hemisphere.

Effect of Foreign Metals on the Rolling of Zinc. E. Prost and A. VAN DE CASTEELE. (Bull. Soc. Chim. Belg., xxvii, 175.)—Ingots weighing 40 pounds were prepared by casting together zinc alloys of various metals, with spelter containing lead 1.05 to 1.25, cadmium 0.076 to 0.11, and iron 0.03 to 0.039 per cent. The conclusions are: Cadmium is harmful above 0.25 per cent.; with 0.5 per cent. rolling is impossible. Arsenic: 0.02 per cent. markedly increases the hardness, and with 0.03 per cent. the metal is too brittle for practical purposes. Antimony is less objectionable than arsenic as regards hardness, as 0.07 per cent. does not increase the hardness; but 0.02 per cent. is enough to produce a striated surface on the rolled sheet, which makes it unsalable. Tin is objectionable when above 0.01, and prohibitive at 0.03 per cent. Copper has no hardening effect until it reaches 0.08, and with 0.19 per cent. the zinc is unworkable. Iron: 0.12 per cent. is a permissible maximum, but this is easily reduced in refining. Lead: Though I to 1.25 per cent. does not interfere with the rolling, a slight increase not only seriously affects malleability, but the excess of lead remains unalloyed and forms patches on the sheet. The presence of two or more impurities together results in a combination of the injurious effects of each.

Copals from Mozambique. Anon. (Bull. Imp. Inst., xi, 221.) The results of the examination of nine samples of "recent" copals (i.e., from existing trees) are given. Most of the samples were of poor quality and too soft to produce satisfactory varnishes, but the 'Mgeji" copal from trees growing in the Madanda forest was of good quality. Four grades of this copal were supplied and they were valued at about \$25.00, \$21.00, \$12.50, and \$6.25 respectively. They were not completely soluble in alcohol, ether, chloroform, benzene, or oil of turpentine; practically insoluble in a mixture of benzene and oil of turpentine, but partially soluble in mixtures of alcohol and ether, alcohol and benzene, and alcohol and oil of turpentine. They all became soluble in oil of turpentine on "melting" for 1½ hours, and in this process lost 14, 16, 21, and 30 per cent. respectively in weight. Varnishes prepared by dissolving the melted copals in oil of turpentine gave almost colorless, hard and glossy coatings in the case of the two more valuable grades, and pale yellowish-brown coatings in the case of the other two.

Variable-speed Aëroplanes. G. DE SAINT-AUBIN. (Comptes Rendus, clvi, 1131.)—This suggests the use of auxiliary planes carried on each side of the ordinary planes, and pivoted on horizontal axes passing through the centres of pressure. These auxiliary planes would be free on these axes when flying at high speeds, and thus would not have any supporting action. On descending, or when at low speeds, they would be controlled and act as extensions of the main planes.

Applications of Calcium. Anon. (Brass World, ix, 9, 317.)— From The Ironmonger: At the recent Foundry Exhibition at Leipzig a display of metallic calcium, as used for improving and purifying molten metals, was exhibited by the Bitterfeld Electro-Chemical Works. Metallic calcium, produced by an electrolytic process from molten calcium chloride, is industrially applied as an energetic purifying agent. It combines with oxygen, nitrogen, and hydrogen with rise of temperature; this increases the temperature of the molten bath and causes vigorous ebullition, whereby the gases, oxides, and portions of slag, dissolved or mixed with the bath, are brought to the surface. This complete purification produces a denser casting with a homogeneous texture. As calcium does not alloy with iron, but always goes into the slag, an excessive addition does not become injurious, as is the case with aluminum and other purifiers. Aluminum readily alloys with iron and causes an abundant separation of graphite which makes the iron pasty. Calcium promotes a thorough mixing and uniformity of the molten bath, thus permitting the use of iron which cannot generally be employed without danger to the good qualities of the product. For the complete deoxidation and refining of a normal melting, an addition of about 50 grammes of calcium per 100 kilogrammes is required. Calcium is also generally recommended for use in the founding of copper and other metals, but then the addition of calcium should not exceed 0.05 per cent. Metallic calcium is sold in airtight tin boxes, as it readily oxidizes on exposure to the air.

The Affinity of Cotton for Dyes. C. Favre. (Bull. Soc. Ind. Mülhouse, lxxxii, 183.)—In printing, and particularly in dyeing, the affinity of cotton for dyes is appreciably diminished by high temperature. This diminution is greater the higher the temperature and the longer the treatment. Steaming under pressure decreases the affinity of cotton for dyes more than high temperature. Mercerized cotton is more affected than ordinary cotton. If the cotton is moist, several hours of steaming under pressure produces only a slight difference in shade. Mordanting with glycerol or glucose protects the cotton, so that light and dark shades can be produced by printing with glycerol, steaming five minutes under 1 kilogramme pressure and then dyeing. Can-drying also weakens the affinity of cotton for dyes.

Absorption of Light by Half-frosted Lamps. A. J. MAKOWER and U. A. OSCHWALD. (Electrician, lxxi, 96.)—Comparisons of the distribution of light from bare and half-frosted lamps of various makes are described. The amount of light absorbed in the lower hemisphere varies according to the structure of the filament, being different in the case of carbon and metal filament lamps; there are considerable variations in the results obtained with different makes of carbon filament lamps. In general, half-frosting reduces the mean hemispherical candle-power by about 10 to 20 per cent.

Manganese-Bronze Castings for Valves. ANON. World, ix, 9, 315.)—Although manganese-bronze is much stronger than ordinary tin bronze, it is unsuitable for valves or other castings required to stand pressure, on account of the dross in the casting. Manganese-bronze cannot be cast without aluminum, the presence of which is absolutely essential for a successful casting. When aluminum, or any alloy containing it, is melted it oxidizes, and the oxide forms dross, through which leakage occurs when pressure is applied. The making of good castings depends upon: (1) The metal must be poured at as low a heat as possible, or at a temperature at which no smoke is given off from the undisturbed surface. If the metal is poured at so high a temperature that it smokes freely, the castings will be full of dross. However, care must be taken that the temperature is not so low that the metal is pasty when poured. (2) The metal must be cast "quietly," without any unnecessary agitation, to avoid exposing new surfaces to the air and causing oxidation which means dross. (3) The gating of the pattern and length of runner are very important. The runner should be as long as possible, so that what dross is in the metal when it enters the mould will remain in it. The use of the horn sprue will insure the best possible castings, as free from dross as possible. (4) Keep the sand as dry as possible, so there will be no bubbling or agitation of the metal when it enters the mould, as when manganese-bronze is agitated dross results. As a matter of economy the manufacture of manganese-bronze castings to stand pressure should not be attempted, but if unavoidable the casting will have to be done and the best made of a "bad job."

Instantaneous Braun-tube Photographs. J. Zenneck. (Phys. Zeitschr., xiv, 226.)—It has lately become possible to take instantaneous photographs of oscillographic curves by means of Braun's kathode-ray tube, owing to the increased luminosity available. The author describes an attachment to an ordinary camera suitable for taking such photographs, and reproduces some fine specimens of results, including that obtained with a damped condenser circuit of frequency 250 per second. The fluorescent substance used was Giesel's zinc sulphide.

New Alloy. Anon. (Met. and Chem. Eng., xi, 8, 438.)—A new alloy, consisting of manganese, titanium, and silicon, has been patented by F. M. Becket, of Niagara Falls, N. Y. It may also contain carbon in proportions varying from a fraction of one per cent. to sufficient quantity to furnish all or part of the carbon required in the re-carburization of steel. The manganese and titanium together are preferably in excess of 50 per cent. of the alloy. When added to steel the component metals of the alloy are stated to diffuse through the molten mass more uniformly and rapidly than do the corresponding ferro-alloys.

Iron Moulds for Casting Brass. Anon. (Brass World, ix, 9, 305.)—Iron moulds are used in the brass industry, both in the rolling mill and brass foundry. In the rolling mill they are used for casting the brass into plates, rods, bars, billets, and tube-shells which are afterward rolled into sheet, rod, wire, and tubing. In the brass foundry they are used for making ingots. Cast iron is the only available metal for these moulds; semi-steel, malleable iron, and steel castings have all been tried, but all fail to give the service and all are more expensive. Any kind of cast iron will not answer for these moulds. For a good mould, the essentials are: (1) The mould must be composed of the right kind of iron,—i.e., of a special, soft iron. (2) The mould must have a good surface. (3) The mould must be straight and flat.

If the iron is not soft, the mould will crack, sooner or later. A soft iron stands the heat better and lasts a long time; such an iron is high in silicon and low in combined carbon. The surface of the mould should be smooth and free from flaws or adhering sand. It need not be polished, and a good, smooth casting is satisfactory. Pickling in hydrofluoric acid is frequently resorted to in order to

remove sand, and sand-blasting is good when necessary.

Micarta. Anon. (Amer. Mach., xxxix, 3, 122.)—The Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa., has developed a new material, known as micarta, as a substitute for hard fibre, glass, porcelain, hard rubber, built-up mica, pressboard, raw-hide, moulded compounds, etc. It is used for commutator bushings and brush holder insulation, noiseless gear blanks, conduit for automobile wiring, etc. It is a tan-brown, hard, homogeneous material having a mechanical strength about 50 per cent. greater than hard fibre. It can be sawed, milled, turned, tapped, and threaded, if a sharp-pointed tool is used and the work is done on a lathe. It can be punched in thin sheets only and cannot be moulded. Micarta is not brittle and will not warp, expand, or shrink with age or exposure to the weather; it takes a high polish, presenting a finished appearance. Two grades are made; the one known as "Bakelite micarta" will stand a temperature of 300° F. continuously, or 500° F. for a short time. It is infusible and remains unaffected by heat until a temperature sufficient to carbonize it is reached. It is impervious to moisture and insoluble in practically all of the ordinary solvents. The other grade, known as "No. 53 micarta," has the same mechanical and electrical properties as the "Bakelite micarta," but differs in its chemical and thermal properties.



# **JOURNAL**

OF

# THE FRANKLIN INSTITUTE

DEVOTED TO SCIENCE AND THE MECHANIC ARTS

Vol. CLXXVI

DECEMBER, 1913

No. 6

## HIGH-VOLTAGE ENGINEERING.\*

BY

## F. W. PEEK, JR.,

Consulting Engineer, General Electric Company.

# THE DIELECTRIC CIRCUIT.

It is our work as engineers to devise means of transmitting energy electrically from one point to another point, and of controlling, distributing, and utilizing this energy as useful work. In general, conductors and insulating materials are necessary. Transmission problems are principally problems of high voltage and therefore of dielectrics. The dielectric circuit will be briefly reviewed before some of the problems of high-voltage engineering are taken up. In order that energy may flow along a conductor, energy must be stored in the space surrounding the conductor. In this surrounding space there is a magnetic field which is proportional to the current, and a dielectric field which is proportional to voltage. Energy does not flow unless these fields exist together. If the dielectric field exists alone it is often spoken of as static.

Considering the two parallel wires of a transmission line, the magnetic field is represented by closed circles surrounding the

<sup>\*</sup> Presented at the meeting of the Electrical Section held Thursday, October 23, 1913.

<sup>[</sup>Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.]

Copyright, 1913, by The Franklin Institute.

conductors, the dielectric field by arcs of circles starting on one conductor and ending on the other conductor. These lines of force represent graphically the direction and strength of the field (see Fig. 1).

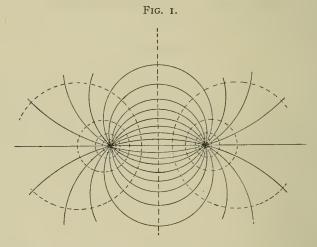
The energy stored in the dielectric field is

 $\frac{e^2C}{2}$ 

and the energy stored in the magnetic field is

 $\frac{i^2L}{2}$ 

The energy stored in the dielectric circuit is thus greater for high voltage, and in the magnetic circuit for high currents. It is



the see-saw of this energy from one form to another that causes all high-frequency troubles, surges, etc.

When energy was first transmitted, low voltages and high currents were used. The magnetic circuit and magnetic field in this way became known to engineers, and as little trouble was had with insulation, the dielectric field was therefore not generally understood. If insulation broke down, its thickness was increased without regard to the dielectric circuit.

A magnetic circuit would not be built in which the magnetic lines were overcrowded in one place and undercrowded in another place,—in other words, badly out of balance. In these days

of high voltages, it is of even more importance to properly proportion the dielectric circuit. Although an unbalanced magnetic field may mean energy loss, an unbalanced or too highly saturated dielectric field will mean broken-down insulation.

The dielectric and magnetic fields may be treated in a very similar way. For instance, to establish a magnetic field a magnetomotive force is necessary; to establish a dielectric field an electromotive force or voltage is necessary. If in a magnetic circuit the same flux passes through varying cross sections, the magnetomotive force will not divide up equally between equal lengths of the circuit. Where the lines are crowded together the magnetomotive force per unit length of magnetic circuit will be larger than where the lines are not crowded together. The magnetomotive force per unit length of magnetic circuit is called magnetizing force. Likewise for the dielectric circuit where the dielectric flux density is high a greater part of the electromotive force per unit length of circuit is required than at parts where the flux density is low. Electromotive force or voltage per unit length of dielectric circuit is called electrifying force, or voltage gradient. If iron or material of high permeability is placed in a magnetic circuit the flux is increased for a given magnetomotive force. If there is an air gap in the circuit the magnetizing force is much greater in the air than in the iron. If a material of high specific capacity or permittivity, as glass, is placed in the dielectric circuit, the dielectric flux is increased. If there is a gap of low permittivity, as air, in the circuit, the gradient is much greater in the air than in the glass.

A given insulation breaks down at any point when the dielectric flux density at that point exceeds a given value. It is thus important to have uniform density. The flux depends upon the voltage, the permittivity, or specific capacity of the insulation and the spacing and shape of the terminal. That is,

$$\Psi$$
 =  $Ce$ 

The flux density at any point is proportional to the gradient or volts per cm. at that point, and to the permittivity of the dielectric. Thus

$$D = \frac{de}{dx} Kk = gKk \tag{1}$$

also

$$D = \frac{\Psi^{\bullet}}{A}$$

As the density is proportional to the gradient, insulations will therefore also rupture when the gradient exceeds a given value; hence if the gradient is measured at the point of rupture it is a measure of the strength of the insulation. The strength of insulation is generally expressed in terms of the gradient rather than flux density.

The gradient may be thought of as a force or stress, and the flux density as a resulting electrical strain or displacement. Permittivity, then, is a measure of the electrical elasticity of the material. Energy is stored in the dielectric with increasing force or voltage and given back with decreasing voltage. Rupture occurs when the force or gradient exceeds the elastic limit. Of course, this must not be thought of as a mechanical displacement. In fact, the actual mechanism of displacement is not known.

When two insulators of different permittivities are placed in series with the same flux passing through them, the one with the lower permittivity or less electrical elasticity must take up most of the voltage,—that is, the "elastic" one may be thought of as "stretching" electrically and putting the stress on the electrically stiff one.

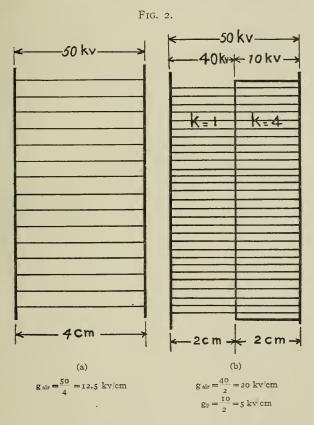
For instance, take two metal plates in air as in Fig. 2 and apply potential between them until the flux density is almost sufficient to cause rupture. Now place a thick sheet of glass between the plates; the capacity and therefore the total flux is increased. This increases the stress on the air, which breaks down or glows. The glass does not break down. Thus by the addition of insulation the air has actually been broken down. This takes place daily in practice in bushing, etc., and the glow is called static.

It is especially important in designing leads and insulators immersed in air to avoid overstress on the air.

It can be seen that specifying volts and thickness does not tell the stress on the insulation. The stress on insulation does not depend altogether upon the voltage, but also upon the shape of the electrodes; as, for instance, for needle points—the flux density at the point must be very great at fairly low voltages, while for large spheres a very high voltage is required to produce high flux density. For this reason 200 kilovolts will jump 50 cm. between needle points, while it will only jump about 17 cm. between 12.5 cm. spheres. From the above it can be seen that it is much more important to design the dielectric cir-

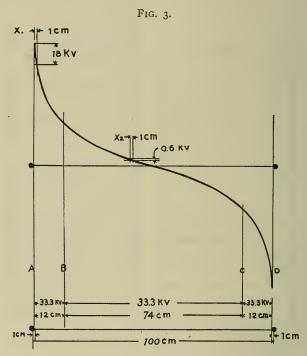
cuit for proper flux distribution than the magnetic circuit. Local overflux density in the magnetic circuit may cause losses, but local overflux density in the dielectric circuit may cause rupture of the insulation.

Consider now the two conductors of a transmission line with voltage between them. The dielectric flux begins on one



conductor and ends on the other conductor (see Fig 1). The flux is very dense at the conductor surface and less so at a distance from the conductor. Hence the voltage gradient is greater at the surface, and breakdown must first occur there. For the particular case shown in Fig. 3 one-third of the voltage is taken up by the space 12 cm. from each conductor, although the total space is 100 cm. The gradient is greatest at the wire surface. That is,

if across a small distance,  $X_1$ , the voltage is measured near the wire surface and then again across the same space  $X_2$  some distance from the wire, it is found that the voltage is much higher across the small space  $X_1$  near the wire surface than across the one further out (Fig. 3). In actually measuring the gradient, or rather calculating it, X is taken very small or dx. The voltage



Distribution of potential in space between wires of a transmission line.

across dx is de. The purely mathematical expression for the gradient at the surface of parallel wires is:

$$g = \frac{de}{dx} = \frac{e}{2r \log_e \frac{s}{r}}$$

If the conductors are close together a spark jumps across when the voltage is high enough to produce overflux density at the conductor surface; or corona and spark-over are simultaneous. If far apart, corona forms around the conductor surface and sparkDec., 1913.]

over only takes place at some higher voltage. The condition for spark-over or corona is as follows: Corona is conducting. When it forms it, in effect, increases the size of the conductor. If this increase of conductor size lowers the flux density, the breakdown remains local. If the increase of conductor size increases the flux density or stress, the breakdown must extend across or spark-over takes place. If  $\frac{s}{r}$  is large, corona forms out to a point where the flux density is below the breakdown density and stops. If  $\frac{s}{r}$  is small, below a critical value, a spark jumps because the corona starts at breakdown flux density and continues on across, as it never reaches a value lower than the breakdown value. The surface gradient at spark-over may, therefore, also be used to measure dielectric strength if the conductors are close enough together so that corona cannot form, or rather spark-over and corona are simultaneous.

#### INSULATION.

As voltages or electromotive forces become higher the proper shaping and spacing of the conductors to prevent dielectric flux concentration becomes of more importance. Three general types of insulation are used,—gaseous, liquid, and solid. The gaseous insulation, air, is the most universal insulation. It is often part of the insulation when not generally realized. For instance, in the line insulator the air is as much a part of the insulator as the porcelain, as the dielectric flux passes through both, and it is important to so proportion the porcelain part that the air is not overstressed. Transformer oil is the most common liquid insulation. The most common solid insulations are treated and varnished paper and cloth, natural and synthetic gums and resins, mica, oiled linen, pressboard, porcelain, glass, rubber, wood, etc. The mechanism of breakdown of the most common insulations of the different types will be considered.

# Gascous Insulation—Air.

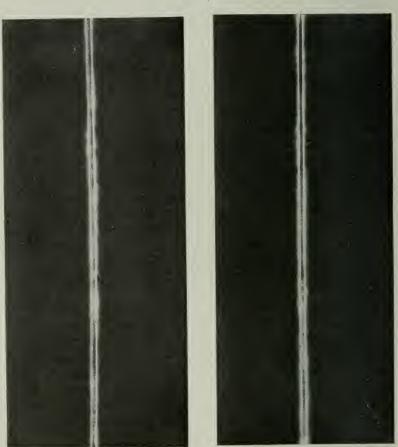
Air is the principal insulation of transmission lines; the socalled line insulators are used for mechanical support. When the voltages were below about 60,000 the conductors used had sufficient radius or circumference so that the surface flux density or gradient was not sufficient to cause breakdown. As voltages became higher the sizes of conductors remained about the same, and, therefore, the flux density or gradient became greater. The

Vol. CLXXVI, No. 1056-44

air broke down, causing the so-called corona and loss. This led to extensive investigation.

When potential is applied between the two conductors of a transmission line and gradually increased, the first evidence of

Fig. 4.



Corona on parallel polished wires.

stress is, if it is dark, glow or brushes at local points where dirt may be on the wire. Wattmeters in the circuit begin to indicate loss. As the potential is increased the whole line very suddenly begins to glow. There is a hissing noise. This point is the visual critical corona point. It is quite definite and decided (see Fig. 4).

The breakdown is extremely sudden. An odor of ozone is noticed near the conductors. The inert oxygen of the air,  $O_2(O=O)$ , is torn apart as active or atomic O. It recombines as  $O_2$  and  $O_3$ 

or ozone. If there is organic matter near, it becomes

oxidized. The metal also becomes oxidized. At higher voltages the nitrogen of the air combines with the oxygen. Wattmeters





Corona on line.

No. 3 o cable. 310 cm. spacing—230,000 volts.

in the circuit show that the loss now increases very rapidly with increasing voltage.

The surface flux density or the gradient at which visual corona starts or breakdown occurs is higher for small conductors than large ones,—that is, air around small conductors has an apparently greater strength than around large conductors (see Fig. 6). If the potential between parallel wires is increased to the value where corona just starts, and this voltage is found to be

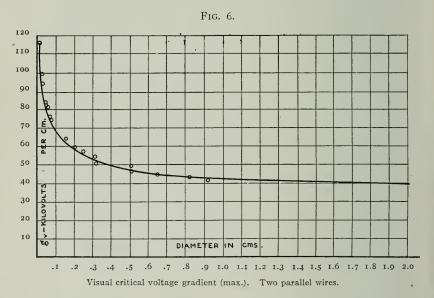
 $e_v$ , the surface gradient or gradient at point of rupture is a measure of the apparent strength of air. This gradient is:

$$g_{v} = \frac{e_{v}}{r \log_{e} \frac{s}{r}} \tag{1}$$

The approximate gradient at any point X cm. from the centre of the conductor is:

$$g = \frac{e_{v}}{X \log_{e} \frac{s}{r}} \tag{2}$$

where s is the distance between centres in cm. and r is the conductor radius in cm.  $e_v$  is kilovolts to neutral. The a-c wave



shape must always be known, as it is the maximum value of the wave upon which break-down depends.

We have found by measuring  $g_v$  for different sizes <sup>1</sup> of wire that the following law holds:

$$g_{v} = g_{o} \left( \mathbf{I} + \frac{0.301}{1 r} \right) \tag{3}$$

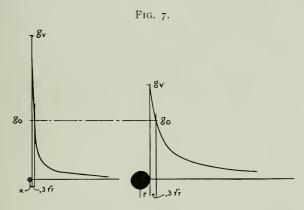
<sup>&</sup>lt;sup>1</sup> "Law of Corona and Dielectric Strength of Air," I, II, III (F. W. Peek, Jr.), *A.I.E.E.*, June 1911, 1912, 1913.

Equating (1) and (3),

$$g_o\left(1 + \frac{0.301}{1/r}\right) = \frac{e_v}{r \log_e \frac{s}{r}}$$

$$g_o = \frac{e_v}{(r + .301 \sqrt{r}) \log_e \frac{s}{r}} = \text{constant} = 30 \frac{\text{kv.}}{\text{cm.}}$$

Thus  $(r+.301^{+}r) = X$  in (2) or  $g_0$  is the gradient .301 r cm. from the surface of the conductor at breakdown. This means that at breakdown the gradient is always constant and equal to  $g_0 = 30$  kv./cm. (max.) at .301 r cm. from the conductor sur-



go is constant at distance .3 | r cm. from surface of wire.

face, independent of the size of the conductor, and is shown graphically in Fig. 7 for both a small and large wire. The explanation seems to be that the strength of air is constant and equal to 30 kv./cm., but that energy is necessary to start rupture, and, therefore, rupture cannot start at the surface, but only after the surface gradient has been increased to  $g_v$ , in order to store the rupturing energy between the conductor surface and .301  $v_r$  cm. away in air, where the gradient is  $g_o$ .  $g_v$  is thus the apparent strength.

Theoretically,  $g_0$  should vary directly with the air density, or

$$g_{o}^{1} = \delta g_{o}$$

If the energy theory is true, the energy storage distance should also vary with  $\delta$ . It has been found that

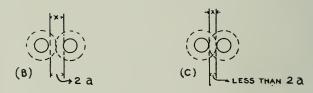
Energy storage distance = .301 
$$\sqrt{\frac{r}{\delta}}^2$$
  $\delta$  is the relative air density.  $\delta = \frac{3.92b}{273 + t}$ 

where t = temperature in degrees C., and b = barometric pressure in cm. of mercury.  $\delta = 1$  at 25° C. and 76 cm. barometer.

Therefore  $g_r$  does not vary directly with  $\delta$ , but

$$g_{v} = g_{o} \delta \left( 1 + \frac{.301}{1 - \delta r} \right) \frac{\text{kv.}}{\text{cm.}} \text{max.}$$
 (4)

The effect is the same whether  $\delta$  is varied by change in temperature Fig. 8.



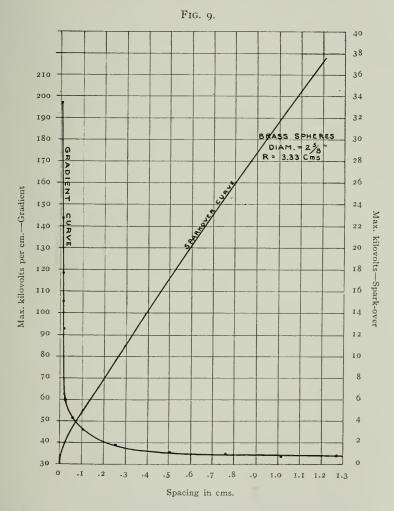
or pressure (over range where there is still no chemical change due to temperature).

According to the above theory,  $g_v$  is independent of the spacing. If, however, the wires are spaced very close together, so as to interfere with the free energy storage distance,—that is, in the order of .301  $\sqrt{r}$  cm. (Fig. 8),— $g_v$  should increase so that sufficient energy to start rupture may be stored in the limited distance. This is actually the case, and, for small spacing, very high

<sup>&</sup>lt;sup>2</sup> "Law of Corona," II, III (F. W. Peek, Jr.), A.I.E.E., June 1912, 1913.

 $g_v$  values have been reached. Fig. 9 shows this effect on 3.33 cm. spheres.

The electron theory may also be very well applied in agreement with the above. Briefly:



When low potential is applied between two conductors any free ions are set in motion. As the potential, and, therefore, the field intensity or gradient, is increased the velocity of the ions increases. At a gradient of  $g_0 = 30$  kv./cm. ( $\delta = 1$ ) the velocity

of the ions becomes sufficiently great over the mean free path to form other ions by collision. This gradient is constant and is called dielectric strength of air. When ionic saturation is reached at any point the air becomes conducting and glows, or there is corona or spark.

Applying this to parallel wires, when a gradient  $g_v$  is reached at the wire surface any free ions are accelerated and produce other ions by collision with molecules, which are in turn accelerated. The ionic density is thus gradually increased by successive collision until at 0.301 1 r cm. from the wire surface, where  $g_0 = 30$ , ionic saturation is reached, or corona starts. The distance 0.301  $v_r$  cm. is, of course, many times greater than the mean free path of the ion, and many collisions must take place in this distance. Thus for the wire corona cannot form when the gradient of  $g_0$  is reached at the surface, as at any distance from the surface the gradient is less than  $g_0$ .

The gradient at the surface must therefore be increased to  $g_v$  so that the gradient a finite distance away from the surface  $(0.301\sqrt{r} \text{ cm.})$  is  $g_o$ . That is to say, energy is necessary to start corona, as explained above.  $g_o$ , the strength of air, should vary with  $\delta$ ;  $g_v$ , however, cannot vary directly with  $\delta$ , because, with the greater mean free path of the ion at lower air densities, a greater "accelerating" or energy distance is necessary. In the equation  $a = 0.3011 \ r/\delta$ ; that is, a increases with decreasing  $\delta$ .

When the conductors are placed so close together that the free accelerating or energy storage distance is interfered with, the gradient  $g_r$  must be increased in order that ionic saturation may be reached in this limited distance.

Tests made over a fairly wide frequency range show little effect of frequency on the starting point of corona on wires, or spark-over on spheres, if highly polished. For needle points, rough surfaces, etc., local corona starts at low voltages at any frequency. At low frequency the loss in the brush is very low and the starting point not much affected. At very high frequency the local loss may be so great that hot needle-like streamers extend out, weakening the air in their path. The needle gap spark-over voltage for continuous high frequency is thus made much lower than the 60-cycle spark-over. The sphere is affected to much less extent.

In high-frequency conductors care should, therefore, be taken

to polish the surface, as any little point will start a "spark needle." which may then play anywhere over the surface or cause spark-over at very low voltage.

The voltage at which visual corona starts between polished parallel wires may be accurately calculated from the following formula:

$$e_v = g_v r \log_v \frac{s}{r}$$
 kilovolts to neutral<sup>3</sup>

where

$$g_v = 30 \, \delta \, \left( 1 + \frac{.301}{1 \, \delta_r} \right) \frac{\text{kv.}}{\text{cm.}} \text{ (max.)}$$

$$g_v = 21.2 \, \delta \left( 1 + \frac{.301}{1 \, \delta_r} \right) \frac{\text{kv.}}{\text{cm.}} \text{ (effective (sine wave) )}$$

The appearance of corona is different on the positive and negative wires. Fig. 10 shows a–c corona on positive and negative parts of the wave.

It becomes of great importance in the design of high-voltage transmission lines to know the various factors which affect corona formation and loss. Loss begins at some critical voltage, which depends upon the size and spacing of line conductors, altitude, etc. For practical transmission lines and frequency near  $60 \, \infty$  the corona loss can be expressed by the equation:

$$p = a f (e - e_{o})^{2} \times 10^{-5}$$
 (5)

where

p = loss in kilowatts per kilometre of single line conductor.

e = effective value of the voltage between line conductors and neutral in kilovolts.

f = frequency.

$$a = \frac{344}{\delta} \sqrt{\frac{r}{s}}$$

r = radius of conductors in cm.

s =spacing between conductors.

 $\delta$  = air density factor.

 $e_o =$  effective disruptive critical voltage to neutral in kilovolts.

$$e_o = m_o g_o \delta r \log_o \frac{s}{r}$$
 kv. to neutral.<sup>3</sup>

<sup>\*</sup>Kilovolts between lines divided by 2 for single-phase and 1'3 for three-phase. In terms of maximum, or effective sine wave depending upon value of  $g_r$  used,

<sup>&</sup>lt;sup>4</sup> "Law of Corona," I (F. W. Peek, Jr.), A.I.E.E., June, 1911. Developed by the author, 1910. Discussion, A.I.E.E., Jan., 1911.

 $g_0$  is the disruptive gradient of air; for all practical sizes of conductor it is constant and is 21.2 kv./cm. (eff.) [wave is assumed close to sine in these formulæ].

 $m_a$  is a constant dependent upon the surface condition.

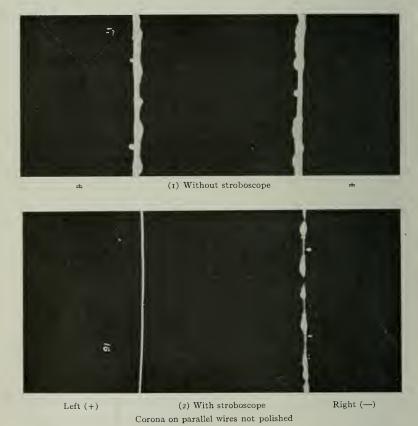
 $m_{o} = 1$  for polished wires.

 $m_a = 0.98$  to 0.93 for roughened or weathered wires.

 $m_{o} = 0.87$  to 0.83 for cables.

Fig. 10a.

No. 13 B. & S. wire. Spacing 12.7 cm. Volts 82,000



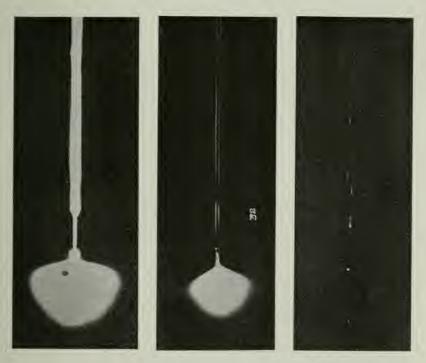
Visual corona does not begin at the disruptive critical voltage  $e_0$ , but always at a higher voltage  $e_v$ . While, theoretically, no loss of power should occur below  $e_v$ , some loss does occur, due to brush

discharge at irregularities of the wire surface, dirt, etc. Practically, however, due to dirt and irregularities the loss starts at  $e_0$  and follows the quadratic law given above even between  $e_v$  and  $e_0$  with sufficient accuracy for practical work. It is interesting to note that the loss below  $e_v$  due to chance brushes, dirt, etc., actually follows the probability curve:

$$p_1 = q\varepsilon - h(\epsilon_o - \epsilon)^2$$

but this need not be considered in practice, as the loss below  $e_v$  is unstable because it depends upon varying irregularities. The

Fig. 10b.



Without stroboscope ± With stroboscope + With stroboscope -One of two parallel polished steel rods pointed at ends. Diameter 0.325 cm. Spacing 10 cm.
Volts 180,000.

storm loss really fixes the maximum operating voltage below  $e_0$ . Equation (5) more than covers the practical transmission range of conductor diameter and spacing, etc. A more com-

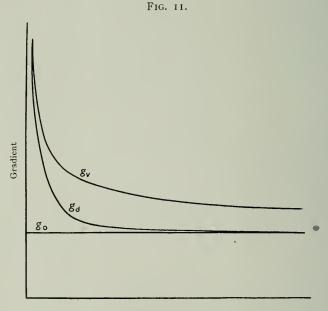
plete equation for use at lower frequency and also for very small conductors or over greater range in any way is:

$$p = 241 (f + 25) \sqrt{\frac{r + \frac{6}{s} + .04}{s} (e - \epsilon_d)^2 10^{-5}}$$

$$e_d = g_d r \log_e \frac{s}{r} \qquad \text{(See Fig. 11.)}$$

$$g_d = g_o \left( 1 + \frac{.3}{1 r} \frac{1}{1 + 230 r^2} \right)$$

Where r is large (above 0.2 cm.) practically  $g_d = g_o$ , and where r is zero  $g_d = g_v$ .

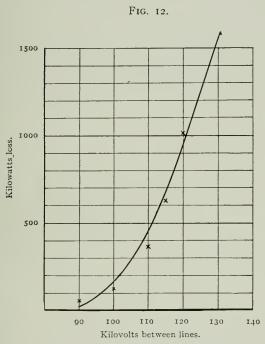


Radius of wire.

For practical frequencies around 60 cycles, and practical sizes of conductor, (5a) thus reduces to the simple equation (5).

Rain and snow lower  $c_0$  and increase the loss. The storm loss can be approximated by taking  $c_0$  in (5) at 80 per cent. of the fair weather  $c_0$ .

As stated above it is generally not advisable to operate above the fair weather  $e_0$  voltage, as the storm loss then becomes excessive. Fig. 12 shows agreement of measured and calculated loss on practical lines. The calculation is made from formula (5). Fig. 13 shows comparison of fair weather and storm loss.



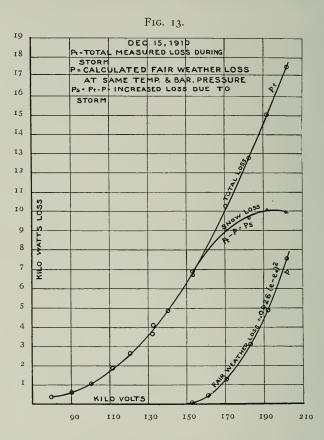
Comparison of calculated and measured losses. x, Measured values. Drawn curve calculated from author's corona formula (5). Diameter wire, 0.375 inch (No. o cable). Spacing, 124 inches. Three-phase. Line length, 63.5 miles. Barometer, 23.8 inches. Temperature, 51° F. This test for corona was made on Shoshone-Leadville transmission line by Mr. G. Faccioli. Test made on operating line three-phase and at high altitude. The check is interesting because of the number of variables taken into account.

### Oil.

In pure oil, as in air, there is no appreciable loss until local rupture, as brush discharge or corona, occurs. The occurrence of brush or corona is extremely sudden. Oil is, therefore, a very desirable insulation, as it can be operated fairly close to its breakdown voltage without heating and consequent lowering of the breakdown voltage.

The mechanism of breakdown in the liquid oil is very similar to that in the gas air. If two very small parallel wires are placed

in clear oil and the voltage is increased, a point is finally reached when glow appears just as corona in air. It appears to extend farther out than the corona in air, and is much less regular. It is much more difficult to detect the starting point than in air, and unless the conductors are very small or far apart (s/r) large)



corona cannot be seen before spark-over. The strength of oil has been measured on spheres of different sizes, and also on wires in the centre of a cylinder. As for air, the *apparent* strength of oil is greater around small conductors than large ones. For spheres and wires the apparent strength takes the form

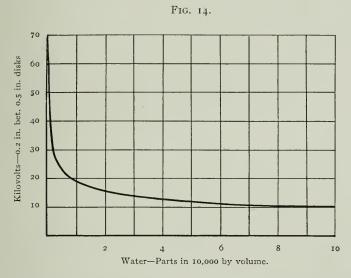
$$g_v = g_o \left( \mathbf{1} = \frac{a}{1 - R} \right)$$

The rupturing energy is much greater for oil than for air. The energy distance is, therefore, also greater—from four to ten times.

The absence of corona, or, rather, the simultaneous appearance of corona and spark-over, unless the wires are very small or far apart, seems to confirm the theory of large rupturing energy distance. Thus, as the voltages increase, corona rupture occurs out to the energy distance; this in effect increases r to such an extent that

$$\frac{s}{r + \text{energy distance}} = \frac{s}{r_1}$$

is less than the ratio at which corona can form.



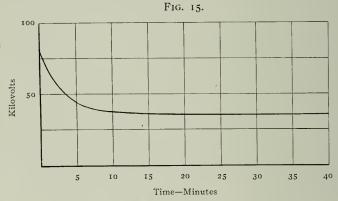
At small spacings, less than the energy distance, the *apparent* strength of oil is also increased. For instance, for 6.7 cm. spheres the breakdown gradient is  $g_v = 100 \text{ kv./cm.(eff.)}$ . At spacings less than the energy distance values as high as 700 kv./cm. have been reached. When oil is used as an insulation the apparent strength is greatly increased by barriers of pressboard, etc.—first, by limiting the energy distance; second, by preventing dirt particles from lining up.

The smallest amount of water greatly decreases the strength of oil (see Fig. 14). Water is, also, always attracted to points of

maximum flux density in order to increase the stored energy. Thus the most highly stressed part is weakened. It is extremely important to remove all moisture from oil in electrical apparatus. This is fairly simple with the filter press oil dryer.

### Solid Insulation.

In air and oil (at moderate frequency) a gradient not greatly under the breakdown gradient may be applied and held, and the loss is so small that no appreciable heating results. The loss in air and oil is thus essentially a phenomenon above the elastic limit. This loss generally exists in some locally brokendown part of the insulation, as corona on the surface of a wire.



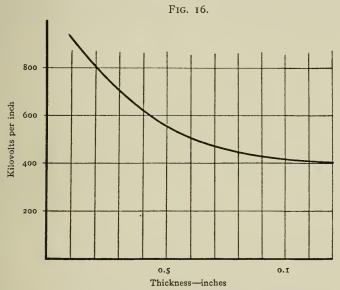
Time test-0.94-inch oiled pressboard (Hendricks).

The break does not extend through the whole insulation, and when the stress is removed new air or oil takes the place of the broken-down insulation.

Almost all insulations are partially conducting or have a high resistance, which is spoken of as "insulation resistance." This apparently has no direct connection with the dielectric strength, which is measured by the gradient or flux density required to *electrically* strain the dielectric above the *electrical* "elastic limit." For instance, in a condenser made of two metal plates with a solid dielectric between them, when a-c potential is applied energy is stored in the dielectric by electrical displacement at increasing potential and delivered back to the circuit at decreasing potential, so long as the potential does stress the insulation beyond the elastic limit. If the dielectric were perfect a watumeter in the circuit

would indicate no loss. In all practical solid insulations there is an  $I^2R$  loss and a dielectric loss, sometimes called dielectric hysteresis. This loss takes place in solids below the elastic limit.

In solid dielectrics a stress may be applied below the elastic limit and after a short time, on account of heating, and hence weakening, rupture will occur. In all solid insulations the time of application must, therefore, be known. The "instantaneous" breakdown voltage is generally four or five times the voltage at which the insulation will operate indefinitely.



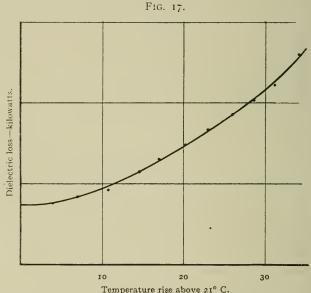
Variation of apparent dielectric strength with thickness— 4.0-inch disks (Hendricks).

In making comparative tests on solid insulations it is generally convenient to make some arbitrary time tests which include the effect of dielectric loss, and thus heating, on the breakdown voltage. The effect of loss is cumulative. The insulation becomes warm and the loss increases with the temperature. The dielectric strength generally decreases with increasing temperature. The ultimate strength depends, naturally, upon the rate at which heat is radiated or conducted away. As an example, for a certain insulation and given terminals, if the voltage is applied "instantaneously,"—that is, increased at fairly rapid

Vol. CLXXVI, No. 1056-45

rate before heating occurs,—80 kv. is required to cause rupture. If 50 kv. is applied, rupture occurs in four minutes. Thirty kilovolts may be applied indefinitely (under the fixed conditions of test) (see Fig. 15).

One of the arbitrary practical tests for comparing insulation is the one-minute time test. In this test the "instantaneous" breakdown voltage is found. Seventy-five per cent, of this voltage is applied for one minute; if breakdown does not occur the



Dielectric loss in a 3750 kva.-120 kv. transformer at 60 cycles (Lewis).

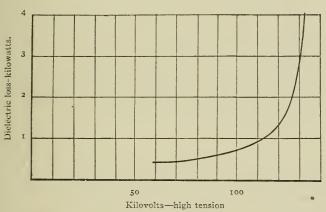
voltage is increased 5 per cent., and one minute allowed to elapse; this is repeated until breakdown occurs. Insulation tests are generally made for convenience between flat terminals in oil.

For a given insulation the puncture voltage per unit thickness  $\left(\frac{e}{x}\right)$  is always greater for thin sheets than for thick ones (see Fig. 16). This is due partly to better heat distribution in the thin sheets, partly due to the fact that energy is necessary for disruption and that the energy distance is limited in the thin sheets, and partly due to flux concentration at the edge of the plates. With flat plates the apparent strength of insulation decreases with increasing area approximately along the probability curve.

Laminated insulation is much better than solid insulation, as weak spots cannot line up in laminated insulation, and it is more uniform. The energy distances are also probably limited by the laminations, and, to some extent, the apparent strength is increased in this way.

It requires energy and, therefore, time to rupture insulations; for a given potential a given number of cycles at high frequency are, therefore, much less injurious than the same number of cycles of low frequency. This also applies to impulse voltages of steep wave front. High frequency is, however, generally very injurious for two very distinct reasons:





Dielectric loss in a 100 kva.-200 kv. transformer at 60 cycles 200 kv.

(1) On account of the very great energy loss at continuous high frequency the insulation may be literally burned up in a very short time, even at low voltages. This condition does not result in practice from surges, etc., on low-frequency lines.

(2) In certain apparatus containing inductance and capacity local very high potential difference may be caused by resonance, and these may cause rupture simply by overpotential.

As energy is required for rupture of insulation, voltages many times in excess of the rupturing voltage may be applied without rupture if the application is very short. Such voltages are generally called impulse voltages of steep wave front. Each impulse, however, permanently damages the insulation, and if a sufficient number are applied rupture occurs.

The energy loss in insulation at constant temperature varies approximately as the square of the voltage. It increases with increasing frequency and temperature (see Figs. 17 and 18).

For air and for oil there is no appreciable loss except at rupture. This may occur as corona, and when the overpotential is removed fresh insulation takes the place of the broken-down insulation—it is self-healing. With solid insulation there is a loss below the rupturing voltage. If local rupture occurs it generally burns the insulation in such a way that the gradient is increased by charring and complete breakdown results. In the case of glass or porcelain a local breakdown generally causes a local mechanical crack which extends across.

#### SOME HIGH-VOLTAGE PROBLEMS.

As important as the quality of the dielectric is the configuration of the electrode and the dielectric. It is also of importance in combining dielectrics of different permittivities to see that one does not weaken the other. It is possible to cause breakdown in apparatus by the addition of perfectly good insulation, dielectrically stronger than the original insulation.

# Causing Breakdown by the Addition of Stronger Insulation.

When insulations of different specific capacities are combined great caution is required, as the addition of a perfectly good and stronger insulation may actually cause complete breakdown. For example, two spheres were set 2 cm. apart in air. At 40 kv. there was no evidence of stress. A 0.2 cm. thick piece of pressboard with a breakdown voltage of 35 kv. (much stronger than air) was then placed between the spheres, making a total insulation of 1.8 cm. of air (38 kv. breakdown voltage) and 0.2 cm. of pressboard (35 kv. breakdown voltage). Complete breakdown of air and pressboard took place immediately, although the voltage was not increased above 40 kv. The direct sum of breakdown voltages is 38 + 35 = 73 kv. (see Fig. 19).

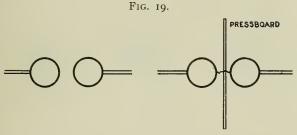
The mechanism of breakdown was as follows: When the pressboard was added, on account of its high permittivity, the flux density was increased to a sufficient extent to cause the air to rupture. This put full voltage (40 kv.) on the pressboard, which in turn ruptured.

### Combining Insulations.

Assume three insulations are available, all of exactly the same dielectric strength, but of permittivity as follows:

Insulation	Α		 	٠.	 	 		 	k = 5.4
Insulation	В		 		 	 		 	k = 3.6
Insulation	С		 		 	 	٠.	 	k = 2.0
Rupturing	gra	adient	 		 	 		 	$g = 100 \mathrm{ky./cm}$ .

As a simple example assume it is desired to insulate a 1.0 cm. wire using 1.75 cm. of insulation with an outside lead covering. The best way of applying the insulation would be so that every part were equally stressed. This ideal cable is impossible with the limited number of k values. The more nearly this condition is realized the higher the voltage that may be applied to the cable without rupture.



Case 1.—If insulation A, B, or C is used alone the breakdown voltage,

$$e_1 = 75 \text{ kv}.$$

Case 2.—Using A next to the wire, then B, then C, in the proper proportions the rupturing voltage is

$$e_2 = 133 \text{ kv}.$$

Case 3.—Using them in the reverse order, C, B, A, the rupturing voltage is

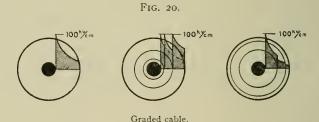
$$e_3 = 63 \text{ ky}.$$

Fig. 20 shows the distribution of stress on different parts of the cable with the three combinations. The areas of the curves are proportional to the breakdown voltages. In Case 2 the insulation of high permittivity may be thought of stretching and putting the stress on the electrically stiffer one B, and so on. In Case 3 the "stiffer" one is next to the conductor, and therefore takes most of the stress.

"Static" and "Leakage" over Insulation.

When one goes into a high-voltage station, sparking is often noticed around the metal parts, etc. This is generally called "static." It is really breakdown of the air caused by overflux density in the air near the metal part, as the metal parts are terminals for lines of force which extend from the high voltages, busses, etc.

Small "static" sparks are also often noticed at fairly low voltages between generator coils and the frame; in the air space between the central terminal and porcelain of a poorly-designed



bushing where the weakest insulation and the one of lowest permittivity is often placed where the stress is the highest, etc. These sparks are caused by overflux density in the air. In the case of the bushing it is sometimes possible to prevent this by short-circuiting the flux through the air, by pasting tinfoil around the inner surface of the porcelain and connecting to the central rod. It is also now taken care of in the best modern high-voltage generators.

When tests are made on insulators or leads, a glow is often seen along the surface of the porcelain or at points on the porcelain. It is often spoken of as "leakage" over the surface. As a matter of fact, it is not really leakage, but due to overflux density in the air. What is called "leakage" or "creepage" over clean porcelain is really breakdown of the air part of the insulator. It is generally not realized that this air is as much a part of the insulator as the porcelain.

### Dielectric Flux Control, Dielectrics in Multiple.

It is sometimes practical to accomplish more with metal than by added insulation. In a case where the field is not uniform, but very much more dense at one point than at another point, the flux may be made more uniform by relieving the dense portion and distributing over the less dense portion by a proper arrangement of metal parts connected to sources of potential of proper value. This is not always practical, as the necessarily complicated potential connections often weaken the apparatus and make it much more liable to breakdown. Metal shields and guard rings may often be used to advantage.

Apparatus must be designed to meet, not only normal conditions, but also, to a reasonable extent, abnormal conditions. Due to surges, lightning, arcing grounds, etc., high frequency. or impulses of steep wave front travel along the line and on reaching apparatus cause local potential rises. This must always be borne in mind. While under ideal normal conditions, with proper flux distribution, it is possible to make the dielectric very thin at points; potential may concentrate at these points at abnormal conditions and cause breakdown. When a dielectric circuit is made up of one dielectric, other dielectrics of different permittivities may be added without changing conditions of stress if added in multiple,—that is, shaped to follow the lines of force. This is, however, not always the best method of combining. Combination should be such as to relieve the weaker insulation and improve conditions by a distribution of stress on the different insulations in proportion to their respective strengths.

## Effect of Altitude on Sparkover of Insulation and Bushings.

The apparent strength of air is reduced almost directly with its density. The density depends upon the temperature and barometric pressure. The density decreases as the temperature increases, and decreases very rapidly with the altitude. Suppose a transformer bushing or line insulator arcs over at 300 kv. where the barometric pressure is 75 cm. At a place where the barometer reads about 60 cm, this same bushing or insulator would arc over at approximately  $\frac{60}{75} \times 300 = 240$  kv. The difference will generally be much less—depending upon design. At still higher altitudes the arc over voltage will be still less. It is, therefore.

very important to consider the altitude when designing high-voltage transformer leads, insulators, etc.

## Methods of Measuring High Voltages.

The needle gap has long been used as a means of measuring high voltage and generally assumed to give correct results. This is not the case, especially at very high voltages, where the error is as much as 20 or 30 per cent.—the needle gap generally indicating higher voltages than really exist. This error is caused by variation due to humidity. There is also another cause of variation of which no mention is made in tables—that due to air density. Due to this cause, a needle gap unless correction is made indicates too high voltages at high altitudes.

The sphere gap is much more reliable.<sup>5</sup> There is no variation due to humidity, and the space factor is smaller than with needle gaps. The air density must, however, be corrected for—but this is fairly simple. It is not a direct function of air density, but also of the radius, as with corona on wires. The constants, however, are not the same. The apparent strength is:

$$g_s = g_o \delta \left( 1 + \frac{k}{\sqrt{\delta R}} \right)$$

Altitude correction is easily made by arranging a table of correction factors for standard spheres at different altitudes.

The sphere should never be used at a spacing greater than 3 R, otherwise corona brush will form before spark-over. It is this brush that causes humidity variation on the needle gap. The gas in the air is probably precipitated to vapor, which has the effect of changing the point to approximate a sphere. The needle gap for this reason requires higher voltages to spark over a given gap at high humidity. The maximum voltages at sea level at which spheres of different diameters should be used on account of spacing is as follows:

Diameter, centimetres.	Grounded.	Non-grounded.
12.5		200
25.	320	380
50.	625	725
100.	1000	1500

<sup>&</sup>lt;sup>5</sup> "The Sphere Gap as a Means of Measuring High Voltages" (F. W. Peek, Jr.), Discussion, A.I.E.E., 1913; G. E. Review, May, 1913.

# Probable Limits of Voltage in Transmission.

It is often asked, What will limit the voltages used in transmission? Transformers have been built and designed up to a million volts. For high voltages the line conductors must be large, otherwise there is a loss due to corona. A quarter of a million volts may be used (except at high altitudes) without excessive diameter or spacing. The line insulator is at present really a more serious limit than corona.6 When the string of insulator units becomes long, the voltages along the string are not balanced, but tend to become higher across the units nearest the line. After a certain string length the addition of units helps very little. This may be pretty well eliminated by redesign. The most serious limit to the insulator, however, is the unreliability or uncertainty of porcelain. The replacement of broken-down insulators is bad, but, worse, every insulator that breaks down weakens the other insulators, transformers, etc., by the production of impulses, high-frequency oscillations, etc. It seems that the real limiting feature will be an economic one; the energy naturally concentrated at any given point will be exceeded by the demand in the surrounding country (except in rare instances) before the transmission distance becomes so great that voltages above the corona or insulator limit are necessary. It seems probable that the whole country could be tied together at about 200 ky. The energy transferred would be the excess at one point to take care of peak at another point, thus keeping the load factor high.

## Voltage Regulation of Transmission Lines.

The actual effective voltage drop due to the reactance in the transmission line or transformer is very small if the power factor of the load is unity. If the power factor is lagging, this drop becomes very large, while if the power factor is leading, this drop is negative or actually adds to the voltage. Use is made of this fact in the control of the voltage. A synchronous motor, running light, is shunted across the line at the load end. If the voltage tends to drop by change of load, the field is changed so as to make the motor require current in the leading direction. If the voltage

<sup>&</sup>lt;sup>6</sup> "Electrical Characteristics of the Suspension Insulator," A.I.E.E., May, 1912.

tends to increase, the field of the motor is changed in the lagging direction. By this means the voltage at the load may be held constant without varying the generator voltage. In fact, the generator voltage is held constant automatically by a Tirrill regulator on the generator field, and the load voltage is held constant automatically by a Tirrill regulator on the synchronous motor field. It is possible by this method to hold the same voltage at both generator and receiving end.

By this means of control the carrying capacity of long-distance, high-voltage transmission lines may be doubled and perfect regulation secured at greater efficiency. Much money may often be saved in this way.

In very long distance, high-voltage lines the condenser or charging current may be as high as the load current. If the load is suddenly lost the voltage at the load end may double, due to this current. The synchronous condensers prevent this by requiring lagging current. In all very long lines this method of control has become a necessity.<sup>7</sup>

## High Reactance in Transformers.

It is desirable to have high reactance in transformers and sometimes to even add external reactance to limit power during a short circuit. It has been objected that this reactance is undesirable from a standpoint of regulation. This is now generally not so. With synchronous motor or phase-control regulation discussed above, reactance is not generally undesirable, but often necessary.

## Arcs and Short Circuits, High-voltage Switching.

Arcs and short circuits, high-voltage switching, etc., produce high-frequency oscillations and impulses of steep wave front. While these transients may in themselves generally not be of very high potential, they travel along the line and upon reaching a piece of apparatus containing inductance and capacity, as a transformer. build up very high voltage inside of the apparatus. This voltage does not appear across the line. The internal high-frequency voltage across a coil may be several times line voltage. A study

<sup>&</sup>lt;sup>7</sup> "Practical Calculations of Long-distance Transmission Line Characteristics," General Elect. Review, June, 1913.

has made it possible to design apparatus in such a way as to limit such disturbances. A special form of protection has also been devised.

These impulses are also sometimes of high voltage, and line insulators may be weakened. It is thus of the greatest importance to see that line construction and insulators are of the very best, and to limit all operations which cause disturbance to the least required number. For this reason it is becoming the practice in modern lines to limit switching as much as possible—especially high-voltage switching. In fact, most of these lines will be arranged without high-voltage bus, and all switching done on the low side. The high side switches will generally be limited to disconnecting switches. A large generating plant will be paralleled on the low side with proper sectionalizing reactances in the bus. The several lines from the high side will be operated as separate systems.

As previously stated, the effect of such impulse voltages is cumulative—each impulse injures the insulation. Everything may thus be apparently all right for years and then a general breakdown may result.

In the above just a few of the problems and tendencies of high-voltage engineering have been touched upon as they have come to mind, without any attempt of going into detail.

The New Quartz-tube Mercury Arc Lamp. E. Weintraub. (Electr. World, 1xi, 984.)—Owing to the difference in the coefficients of expansion of quartz and platinum it is not possible to seal in platinum electrodes. Tungsten electrodes can be sealed in with a special borosilicate glass of high melting-point, and with a coefficient of expansion equal to  $3.4 \times 10^{-6}$ . This answers perfectly and renders it possible to use a higher temperature in the lamp without leakage. A current density three times that customary with platinum electrodes can be used, and the dimensions of the lamp are considerably reduced. The 110-volt lamp is only about 5 inches long. The use of tungsten also enables a solid anode to be used. This renders superfluous the complexities ordinarily considered necessary to balance the difference in evaporation of mercury at the electrodes. The lamps can be conveniently mounted in a vertical position so as to give a high horizontal illumination. The specific consumption of the 220-volt lamp is said to be 0.55 watt per mean spherical candlepower, the 110-volt lamp is rather less efficient. The lamp is being developed for use on alternating circuits and for series lighting.

Physiological Effects of Carbon Monoxide. A. S. MUNROE. (Sch. of Mines Quart., xxxiii, 340.)—One of the most serious dangers from the presence of carbon monoxide in the air of mines is its effect on the health of the workmen who daily inhale small amounts of this gas. The blood, when partly saturated, is less able to perform its proper functions, so that the patient suffers from anæmia and the complications resulting from this weakened condition. According to Edsall, miner's phthisis is due chiefly to carbon monoxide poisoning. Recent observations have shown that for some hours after a blast, under ordinary mining conditions, carbon monoxide may be present in dangerous amounts, and undoubtedly men engaged in sinking, drifting, and stoping, where the circulation of air is deficient, have their blood partially saturated with carbon monoxide the greater part of the time. It is quite certain that dissociation of carbon monoxide from the blood is slow, and that those whose blood is partially saturated will sooner fall victims, where larger quantities of the gas are breathed, than those whose blood is untainted by it. Men who have repeatedly suffered, become very sensitive to the gas, and in most cases are compelled to abandon work in which they must inhale air containing it. The fact that the affinity of carbon monoxide for hæmoglobin is over two hundred times greater than that of oxygen, will give an idea of the slowness of its dissociation from blood containing it, and the great liability to its accumulation.

Determination of Critical Points Arr and Acr by a New Method. J. E. Stead. (Iron and Steel Inst., Sept., 1913.)—Two bars of the steel to be tested, conveniently measuring 115 x 10 x 5 mm., are supported out of contact with each other in a short porcelain tube, which is then inserted in the side of a muffle furnace, so that, while the inner ends of the bar are heated to about 1000° C., the outer ends remain well below 700° C. After about 30 minutes the temperatures, which have then become constant, are ascertained by introducing thin wires of silver, aluminum, zinc, etc., into the passage between the bars, and noting the points at which the wires fuse. A scale giving the temperature at each point along the bars can thus be plotted. The bars are removed, quenched, ground to remove the decarburized skin, immersed in dilute nitric acid, washed in water and alcohol, and dried. The hardened part is then seen to be quite black, while the soft part is gray, the plane of abrupt change indicating the critical point Acr. A method of obtaining the points Arr and Acr at the same time is to heat two bars of the same steel together, and, after the temperature is constant, slowly to withdraw one bar for about 15 minutes, continue the heating for 15 or more minutes, and then, after taking the temperature readings, to quench and etch the bars. The withdrawn bar will give the point Arr. It is stated that this method gives results within 3° C. of the truth.

### PROPORTIONING OF LONG-SPAN TRUSS AND CANTI-LEVER BRIDGES.\*

#### BY

### JOSEPH MAYER.

Assistant Engineer, Quebec Bridge Commission, Montreal, Canada.

#### INTRODUCTION.

The purpose of this paper is to describe a reliable method of finding the most economical general dimensions of long-span ordinary truss and cantilever bridges, and incidentally to give formulas which express their weight as a function of the loads, the unit stresses, and the general dimensions.

In the course of twenty-six years spent in designing bridges, among which were numerous long-span truss, cantilever, and suspension bridges, many rules for finding approximately the most economical dimensions and the weights of details were developed. This paper combines these rules into a logically connected whole and gives, where practicable, the mathematical reasons for them. The formulas are all given with their proofs, so that their truth can be easily tested.

Though many of the formulas appear, on first inspection, complicated, they permit the calculation of the weight of the longest cantilever bridge within a few days with reasonable accuracy, and make it thereby possible to compare the weights of designs with different general dimensions and to select the most economical shape of the trusses in a very short time.

Without such formulas the only practicable way to exactly compare the economy of different designs is by means of stress sheets and estimates which require often more time and labor than is available, and these estimates give very little indication how the general dimensions should be changed to secure the most economical design. The writer, therefore, believes that the method given in this paper is the only explicit method to attain this end, which is not based on mere trained feelings. These latter are only acquired after a lifetime of bridge calculation and are even

<sup>\*</sup> Communicated by the author.

then only roughly approximate guides, reliable only within the range of the experience on which they are based.

MONTREAL, July, 1913.

#### ORDINARY TRUSSES

For the purpose of giving in a compact form the general course of the argument and its useful results the proofs for the formulas used are given in an appendix. The general method followed is to express the weight of the trusses and bracing as functions of the general dimensions of the trusses, the loads, and the unit stresses, and to show thereby the features that govern the weights.

The general formula for the total weight of steel of an ordinary truss span is:

$$W = \text{r.o3} \left[ F + \frac{L^2}{\text{r} - C_d L} \left\{ \mu C_{\mu} + \frac{A_l L}{6} + B_l + C_d f \right\} \right] \cdot \cdot \cdot \cdot \cdot (\text{r})$$
(i) (ii) (iv)

Where:

W = Total weight of steel of span.

F = Total weight of steel in floor.

L = Length of span centre to centre of end shoes in feet.

$$C_d = \frac{\text{o.83}}{\text{I}_2} (AL + 4B)$$
 for parallel chords....(2)

$$Cd = \frac{0.73}{12} (AL + 4B)$$
 for curved top or bottom chords..(3)

For B take

Bv with vertical posts. See (12).

Bi with inclined posts. See (13).

Bk with K-system of web members. See (14).

h = Height of trusses centre to centre of parallel chords.

 $h = 0.93 \times \text{height centre to centre of chords at centre of span with curved top or bottom chords.}$ 

Take  $h = \frac{L}{6}$  for a double-track railway and highway bridge carrying Cooper's E 55 load on each railway track and highways equivalent to one railway track with Cooper's E 55 load.

 $h = \frac{L}{8}$  for a highway bridge with the load on the trusses equivalent to that with a railway track with Cooper's E 18.3 load.

For a bridge with the load on the trusses equivalent to that from one track with Cooper's E p load take

$$h = \frac{L}{8} \left( 1 + \frac{1}{3} \frac{p - 18.3}{146.7} \right)$$
 (5)

$$a_t = \frac{\text{Weight of one panel of tension chord}}{3.4 \times \text{its required net area in square inches} \times \text{length}} \dots$$
 (6)

$$\alpha_c = \frac{\text{Weight of one panel of compression chord}}{3.4 \times \text{its required gross area in square inches} \times \text{length}} \dots (7)$$
of chord for one panel in feet

 $a_t \sim 1.25 \sim a_{t1}$  for eyebars.

∾ signifies "is approximately equal to."

The exact values of  $a_t$  and  $a_{t1}$  (see below) can be found when the length and width of the bars and the diameters of the pins are known.

 $a_t \sim 1.5$  for riveted latticed tension members.

 $U_t = 20,000 = \text{axial unit stress in tension chord from (dead + live + wind) stress for carbon steel.}$ 

 $U_c = 14,000 - \sigma_b = \text{axial unit stress in compression chord for}$   $\frac{l}{r} < 50 \dots (8)$ 

where l = length between supports

and r = least radius of gyration of cross section.

 $\sigma_b$  = bending stress due to weight of member.

$$\sigma_b \sim \frac{l^2}{1.2\ell} \cos \delta \dots$$
 (10)

for continuous top chords where e = distance of extreme fibre in vertical plane from neutral axis, l and e both in feet and  $\sigma_b$  in pounds per square inch.

 $\delta$  = angle of chord with horizontal.

 $\sigma_b \sim \frac{l^2}{0.8e} \cos \delta$  for discontinuous chords with two pin ends... (11)

$$B_v = 4 \left\{ \frac{2 \alpha_{h}}{U_h \sin 2\beta} + \frac{\alpha_{c1}}{U_{c1} \tan \beta} \right\}$$

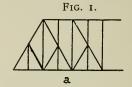
for vertical posts as in Fig. 1 (a) .....(12)

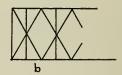
$$B_i = \frac{4.25}{\sin 2\beta} \left\{ \frac{\mathbf{a}_{t1}}{U_{t1}} + \frac{\mathbf{a}_{c1}}{U_{c1}} \right\}$$

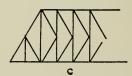
for inclined posts as in Fig. 1 (b).....(13)

$$B_k = 3.75 \left\{ \frac{\alpha_{t1}}{U_{t1}} + \frac{\alpha_{c1}}{U_{c1}} \right\} \left\{ \frac{1}{\sin 2\beta} + \frac{1}{2 \tan \beta} \right\}$$

for K-system of web members as in Fig. 1 (c) ...... (14)







 $\alpha_{t_1} \sim 1.25 \; ; \; \alpha_{c_1} \sim 1.50$ 

 $U_{l_1}$  and  $U_{c_1}$  are the unit stresses of web members for tension and compression respectfully.

For eyebars  $U_{t_1} = U_t = 20,000$ 

For riveted tension members  $U_{t_1} = U_t = 18,000$ 

$$U_{c_1} = 17,500 - 70 \frac{l}{r} - \sigma_b \quad \text{for } \frac{l}{r} > 50.....$$
 (15)

$$U_{c_1} = 14,000 - \sigma_b \quad \text{for } \frac{l}{r} < 50.....$$
 (16)

l = length between supports, e = distance from neutral axis to extreme fibre measured in vertical plane, both in feet.

 $\delta$  = angle of post with horizontal

 $\beta$  = angle of post with vertical

$$\beta = 90 - \delta$$

 $m_r$  = uniform moving load per lineal foot of bridge, giving the same weight of chords as the actual railway moving load; this is approximately the uniform moving load per foot which gives at a distance of  $\frac{1}{4}$  the span from its end the same moment as the actual load, or

where  $M_{r_L}$  is the moment of the actual load at a distance

 $\frac{L}{4}$  from the end of the span.

$$I = \frac{\text{impact stress}}{\text{railway moving load stress}}$$
 (20)

No impact should be taken for highway load  $m_h$ .

$$I = \frac{300}{2L + 300}$$
 for double track.................... (22)

For calculating the sections of the stringers, floor beams, floor-beam hangers, and the truss members carrying one panel or less take

$$i = \frac{300}{\lambda + 300} \dots (23)$$

Vol. CLXXVI, No. 1056-46

where  $\lambda = \text{length of loaded track giving the maximum stress.}$  In calculating the floor the moment and shear from the railway load should be multiplied by (x + i) and the moments and shears from highway load should be added without impact.

$$C_{\mu} = \frac{\circ \cdot 96}{12} (AL + 4B)$$
 for curved top or bottom chords..... (25)

 $B_r$  = width of bridge.

 $p_w^t$  and  $p_w^c$  are the wind pressures in pounds per lineal foot of span for the lateral system between the tension and compression chords of the main trusses respectively.

$$p_w^I = 750 + 0.7L....$$
 (29)

for double-track railway and highway through bridges carrying Cooper's E 55 load on each railway track and highways equivalent to one railway track with Cooper's E 55 load.

For deck bridges with these loads:

$$p_w^c = 750 + 0.7L \dots (30)$$

$$p_w^t = 150 + 0.7L \dots (31)$$

Take  $p_w^c$  and  $p_w^t$  half as large for a highway bridge with the load on the trusses equivalent to a railway track with Cooper's E 18.3 load.

For a through bridge with the load on the trusses equivalent to that from one track with Cooper's E p load take in through bridges.

$$p_w^c = (75 + 0.35L) \left( 1 + \frac{p - 18.3}{146.7} \right) \dots (32)$$

$$p_w^t = (375 + 0.35L) \left( 1 + \frac{p - 18.3}{146.7} \right) \dots (33)$$

For a deck bridge with this load take

$$p_{w}^{t} = (75 + 0.35L) \left( 1 + \frac{p - 18.3}{146.7} \right) \dots (34)$$

$$p_w^c = (375 + 0.35L) \left( 1 + \frac{p - 18.3}{146.7} \right) \dots (35)$$

$$B_l = \frac{6.8 \ p_w \alpha_l}{U_l \sin 2 \ \beta_l} \tag{36}$$

Equation (36) is good only for rigid lateral diagonals.

$$a_l = \frac{\text{Weight of lateral diagonal strut}}{3.4 \times \text{its required gross section in square inches} \times} \dots$$
 (38)

 $U_l$  = Axial unit stress per square inch in lateral diagonal struts.

 $\beta_l$  = angle of lateral diagonal struts with a horizontal line normal to the length of the span.

$$U_l = 17,500 - \frac{70 l}{r} - \sigma_b \text{ for } \frac{l}{r} > 50...$$
 (39)

$$U_l = 14000 - \sigma_b \text{ for } \frac{l}{r} < 5^{\circ} \dots$$
 (40)

For box section lateral diagonal struts made of 4 or 8 angles latticed on four sides with double system of laterals  $a_l = 2.6$  for carbon steel,  $a_l = 3$  for nickel steel.

For short spans where other kinds of rigid diagonal struts are used,  $a_l$  is smaller and must be specially determined.

The values given for  $a_t a_c a_{t1} a_{c1}$  and  $a_l$  were determined from designs for the Quebec bridge now under construction.

f = total weight of floor per lineal foot of bridge in pounds; includes track, flooring, snow and steel.

$$l = 27 + \frac{4L}{300} \tag{41}$$

l = economical average panel length in feet for a double track railway and highway bridge carrying Cooper's E 55 load on each railway track and highways equivalent to one railway track with Cooper's E 55 load.

Take 34 as much for a highway bridge with the load on the trusses equivalent to that with a railway track with Cooper's E 18.3 load.

For a bridge with a load on the trusses equivalent to one track with Cooper's E p load take

$$l = \left(20.25 + \frac{L}{100}\right) \left(1 + \frac{1}{3} \cdot \frac{p - 18.3}{146.7}\right) \cdot \dots (42)$$

In spans of less than 600 feet the panel length is best taken uniform. For longer spans it is advantageous to increase the panel length toward the centre of the span.

In the formula (1) for the total weight of steel in a truss span the factor 1.03 is introduced to cover the end shoes, which weigh about 3 per cent. as much as the steel of the rest of the bridge.

 $\bar{F}$ , the weight of steel in the floor, must be found by designing and estimating the weight of the floor beams and stringers.

The four items in the  $\left\{\begin{array}{c} \end{array}\right\}$  of the formula (1) give, if multiplied by  $\frac{L^2}{1-C_dL}$ , different parts of the weight of the span.

Item (I), 
$$\frac{\mu C_{\mu} L^2}{I - C_d L} = W_{\mu + d}$$
 (43)

gives the weight of the steel required in the trusses to resist the stresses from the moving and impact load plus the total weight of steel needed to carry it.

$$\mu C_{\mu} L^{2} = \mu \left( \frac{AL^{3}}{12} + \frac{BL^{2}}{3} \right) = W_{\mu}$$
 (44)

for parallel chords is the weight of steel needed for meeting the direct stresses from the moving and impact load  $\mu$ .

 $\mu \frac{AL^3}{12}$  is the corresponding weight of steel in the chords;  $\frac{\mu L^3}{12}$  is the moment area by load  $\mu$ . The weight of steel in the chords to meet the direct moving load and impact stresses is therefore equal to "A" multiplied by the moment area due to load  $\mu$ .

 $\mu \frac{BL^2}{3}$  is the weight of steel in the webs to meet these direct stresses from the moving and impact load  $\mu$ .

 $\mu \frac{L^2}{3}$  is the shear area due to load  $\mu$ . The weight of steel in the webs to meet these direct moving load and impact stresses is therefore equal to "B" multiplied by the shear area due to load  $\mu$ .

Item (II)

$$\frac{\frac{\mathrm{I}}{6} \ A_l L^3}{\mathrm{I} - C_d L}$$

gives the weight of steel required in the chords of the two lateral systems to resist the wind stresses plus the total weight of steel needed to carry it.

$$\frac{1}{6}A_lL^3$$

is the weight of steel in the chords of the two lateral systems required to meet the wind stresses.

Item (III)

$$\frac{B_l L^2}{1 - C_d L}$$

gives the weight of steel of the lateral diagonals and the cross bracing plus the weight of steel needed to carry it.

Item (IV)

$$\frac{C_d f L^2}{\mathbf{I} - C_d L}$$

gives the weight of steel needed to carry the floor.

An example will clearly show the procedure for finding the general dimensions and the approximate weight of a long truss span.

Example.—To find the best general dimensions and the approximate weight of a 700-foot span for a double-track rail-

way with Cooper's E 55 load per track.

For finding the best average panel length we use formula (42). With  $p = 2 \times 55 = 110$  we obtain l = 32.93 feet.

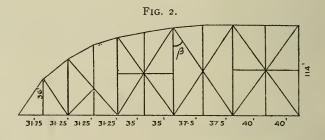
This gives 21 panels.

Formula (5) gives h = 105.75.

$$\frac{h}{0.93}$$
 = 113.7 = maximum height.

At the end posts we need adequate height to make a good portal. For this purpose 36 feet is adequate.

Twenty-one panels are not convenient. If we choose 20 panels and 114 feet maximum height with parabolic top chord we obtain with the panel lengths shown in Fig. 2, a diagram



which gives nearly uniform angles  $\beta$  slightly smaller than 45°, and which is the most economical design or very nearly so. Twenty-two panels might be slightly more economical, but the

difference would be small and could only be found by actually designing both spans.

The weight of this span is given approximately by the general formula (1).

The h to be used in finding A and B is not the height at centre, but 0.93 × this height = 106 feet.

The panel length to be used in the calculation of the weight is the average panel length

$$\frac{700}{20} = 35 \text{ feet}$$

We find

$$\tan \beta = \frac{70}{106} = 0.742$$

$$\beta = 36^{\circ}34'30'' \quad 2\beta = 73^{\circ}9' \quad \sin 2\beta = 0.957$$

The weight of the steel in the floor is found to be 1,100,000 pounds = F.

For the total weight of floor per lineal foot of bridge, we find f = 2570 pounds. Of this, 1000 pounds is the weight of the two tracks and 1570 pounds the weight of the steel.

$$U_c = 14,000 - \sigma_b$$

$$\sigma_b = \frac{35^2}{1.2e} = 500 \qquad \text{from (10)}$$

$$\therefore U_c = 13,500$$

$$U_{c_1} = 12,000$$

$$I = \frac{300}{1700} = 0.1765 \qquad \text{from (22)}$$

$$1 + I = 1.1765$$

$$m_r = 11,340$$

$$\mu = 11,340 \times 1.1765 = 13,340$$

$$A = \frac{3.4}{100} \left\{ \frac{1.24}{20,000} + \frac{1.45}{13,500} \right\} = 5.434 \times 10^{-6}$$
from (4)

$$B_v = 4 \left\{ \frac{2.48}{20,000 \times 0.957} + \frac{1.5}{12,000 \times 0.742} \right\} = 1192.4 \times 10^{-6}$$
 from (12)

$$C_d = \frac{0.73}{12} \left\{ 5.434 \times 700 + 4 \times 1192.4 \right\} 10^{-6} = 521.5 \times 10^{-6}$$
 from (3)

$$C_d L = 0.36505$$
;  $I - C_d L = 0.63495$ 

$$B_r = 35 \text{ feet}$$
;  $\tan \beta_l = \text{i}$ ;  $\beta_l = 45^{\circ}$ 

$$C_{\mu} = 0.08 \times 8573.4 \times 10^{-6} = 685.87 \times 10^{-6}$$
 from (25)

$$\mu C_{\mu} = 13,340 \times 685.87 \times 10^{-6} = 9.15$$

$$p_w^c = \left(75 + 0.35 \times 700\right) \left(1 + \frac{91.7}{146.7}\right) = 520$$
from (32)

$$p_w^{i} = \left(375 + 0.35 \times 700\right) \left(1 + \frac{91.7}{146.7}\right) = 1000$$
from (33)

$$A_l = \frac{3.4}{35} \left( \frac{1.24}{20,000} \cdot 1000 + \frac{1.45}{13,500} \times 520 \right) = 0.01145$$
 from (26)

$$B_l = \frac{6.8 \times 1520 \times 2.6}{13,000 \times 1} = 2.067$$

$$C_dF = 521.5 \times 10^{-6} \times 2570 = 1.340$$

$$\frac{1}{6}A_{l}L = \frac{0.01145 \times 700}{6} = 1.336$$

$$W = 1.03 \left[ 1,100,000 + \frac{490,000}{0.63495} \left\{ 9.15 + 1.336 + 2.067 + 1.34 \right\} \right]$$

W = 12,180,000 pounds = total weight of steel in 700-foot span.

 $\frac{W}{I}$  = 17,400 pounds per lineal foot of span.

Of this 16,900 are distributed over the span. The rest is the weight of the shoes.

The proper dead load to use for the stress sheets is 17,900 pounds per foot of bridge.

If the trusses and bottom laterals were made of nickel steel, 50 per cent. stronger than carbon steel, we would obtain:

$$U_{c} = 21,000 - \sigma_{b}$$

$$\sigma_{b} = 600$$

$$U_{c} = 20,400$$

$$U_{t} = 30,000 = U_{t}$$

$$U_{c_{1}} = 17,000$$

$$A = \frac{3.4}{106} \left(\frac{1.24}{30,000} + \frac{1.45}{20,400}\right) = 3.606 \times 10^{-6}$$

$$B_{v} = 4 \left(\frac{2.48}{30,000 \times 0.957} + \frac{1.5}{17,000 \times 0.742}\right) = 821.1 \times 10^{-6}$$

$$C_{d} = \frac{0.73}{12} \left\{3.606 \times 700 + 3284.4\right\} 10^{-6}$$

$$= 353.3 \times 10^{-6}$$

$$C_{d}L = 353.3 \times 10^{-6} \times 700 = 0.2473$$

$$I - C_{d}L = 0.7527$$

$$C_{\mu} = 0.08 \times 5808.6 \times 10^{-6}$$

$$= 464.69 \times 10^{-6}$$

$$\mu C_{\mu} = (13,340 \times 464.69 \times 10^{-6}) = 6.20$$

$$A_{t} = \frac{3.4}{35} \left\{\frac{1.24}{30,000} \times 1000 + \frac{1.45 \times 520}{20,600}\right\} = 0.00757$$

$$B_{l} = \frac{6.8 \times 1520 \times 3}{20,000} = 1.5504$$

$$\frac{1}{6} A_{l}L = \frac{0.00757 \times 700}{6} = 0.8832$$

$$W = 1.04 \left[ 1,100,000 + \frac{490,000}{0.7527} \left( 6.20 + 0.883 + 1.55 + 1.34 \right) \right]$$

W = 7,900,000 pounds. Of this the floor, the top laterals, the cross bracing, and the shoes are carbon steel, the remainder nickel steel.

Since the shoes are carbon steel and a large part of the span nickel steel, the 3 per cent. does not hold true.

There are approximately 2,200,000 pounds of carbon steel and 5,700,000 pounds of nickel steel, against 12,180,000 pounds carbon steel in the first design.

It is evident that the second design is cheaper.

If the prices of the two steels are given, a short calculation shows which should be used for the floor.

The method of procedure here advocated will greatly abbreviate the finding of the best design and the selection of the proper dead load for the stress sheet. Different designers will find with different specifications slightly different coefficients  $\alpha$  and different weights for the shoes, and they will have to determine the exact value of the coefficients from their own designs.

The correctness of the empirical formulas for the best panel length and the best height, as well as for the wind pressure to be assumed, can be tested from actual designs.

The proofs for the theoretical formulas are given in Appendix A.

#### CANTILEVER BRIDGES.

We found for ordinary trusses with parallel chords that the weight of the chords required by the moving load and impact stresses of a load  $m_r + m_h$  where  $m_h$  is the highway load and  $m_r$  the equivalent uniform railway load, both per foot of bridge, is equal to A multiplied by the moment area of the load.

$$A = \frac{3.4}{h} \left( \frac{\alpha_t}{U_t} + \frac{\alpha_c}{U_c} \right) \dots \tag{4}$$

The load  $m_r + m_h$  was replaced by a uniform load  $\mu$ , giving the same total weight of chords as called for by the highway load  $m_h$ , the railway load  $m_r$ , and the impact produced by the latter.

The weight of the web required by the moving load and impact stresses of the load  $m_r + m_h$  was found to be equal to the shear area of load  $\mu$  per lineal foot of bridge multiplied by B.

B is different, according to the nature of the web system. Three main web systems were considered,—one with vertical posts, one with inclined posts, and one with K system.

The corresponding values of B were called  $B_v$ ,  $B_i$ ,  $B_k$ . We found:

$$B_{i} = \frac{4.25}{\sin 2\beta} \left( \frac{\alpha_{l_{1}}}{U_{l^{1}}} + \frac{\alpha_{c_{1}}}{U_{c_{1}}} \right)$$
 (13)

These formulas also give the weight of the chords and the webs of a cantilever arm with parallel chords required for the moving load and impact stresses of the load  $m_r + m_h$ , as is apparent from their derivation given in Appendix A.  $\mu$  is in this case the uniform load giving the same total weight of the chords of the cantilever arm as the actual load  $m_h + m_r$  with the impact of  $m_r$ . With given height, panel length, and unit stresses, the weight of the trusses required for the stresses from moving load and impact is, therefore, governed by the moment and shear areas of the uniform load  $\mu$  per lineal foot of bridge. These should, therefore, be made as small as possible.

In a cantilever bridge with a main span of length L, a suspended span of length  $l_s$ , two cantilever arms each of length  $l_c$ , and two anchor arms of length  $l_a$ , the moment area of the suspended span for a unit load per foot of bridge is

$$M_s^a = \frac{l_s^3}{12}$$
; its shear area is  $S_s^a = \frac{l_s^2}{3}$ 

The moment area of one cantilever arm is

$$M_c^a = \frac{l_s l_c^2}{4} + \frac{l_c^3}{6}$$

The shear area of one cantilever arm is

$$S_c^a = \frac{l_s l_c}{2} + \frac{l_c^2}{2}$$

The moment area of the main span is

$$M_L^a = \frac{l_s^3}{12} + \frac{l_s l_c^2}{2} + \frac{l_s^3}{3}$$

The shear area of the main span is

$$S_L^a = \frac{l_s^2}{3} + l_s l_c + l_c^2$$

The moment area of anchor arm is

$$M_a^a = \frac{l_c (l_s + l_c) l_a}{4}$$

The shear area of anchor arm is

$$S_a^a = \frac{l_c (l_s + l_c)}{2} + \frac{l_a^2}{6}$$

A short anchor arm with a total anchorage pull positive for all positions of the moving load is assumed.

The total moment area of the three spans is:

$$M_b^a = \frac{l_s^3}{12} + \frac{l_c^2 (3l_s + 2l_c)}{6} + \frac{l_c (l_s + l_c) l_a}{2}$$

The total shear area of the three spans is

$$S_b^a = \frac{l_s^2}{3} + 2l_c(l_s + l_c) + \frac{l_a^3}{3}$$

The formulas for  $M_b^a$  and  $S_b^a$  show that the least weight of trusses for moving load and impact is obtained when  $l_a$  is a minimum.

The anchorage stress from unit moving load per foot of bridge is

$$S_a^{end} = l_c \left( \frac{l_s + l_c}{2l_a} \right)$$

The anchorage stress is a load resisted by the anchorage and carried by the main pier. A short anchor arm gives large anchor stress. This calls for large main piers and large anchor piers and anchorages.

To avoid excessive cost of these, anchor arms about fivesixths as long as the cantilever arms are generally found economical, unless the profile of the river suggests a longer anchor arm to obtain a better site for the anchor piers. The length of the suspended span giving the least moment area of bridge is:

$$l_c = \frac{L - l_a}{4}$$

If 
$$l_a = \frac{5}{6} l_c$$
, we obtain  $l_c = \frac{6}{29} L$ .

The moment area is a maximum for  $l_s = 0$ .

The shear area of the bridge is also a maximum for  $l_s = 0$ , and constantly decreases with increase of  $l_s$  until  $l_s = L$ .

When the suspended span is erected by building out from the ends of the two cantilever arms there arise with long main and long suspended span large erection stresses which govern the sections required in the ends of the cantilever arms and demand large increases in their weight to meet them.

With this method of erection

$$l_s = l_c = \frac{L}{3}$$

gives the most economical bridge for very long main spans.

If the suspended span is erected independently and floated into position, which is for long main spans often the most economical procedure and materially shortens the time required for erection, a considerably longer suspended span becomes economical, especially when the length of the main span is much less than the practical maximum of 1800 feet.

The formula

$$l_c = \frac{L - l_a}{4}$$

for the length of the cantilever arms which gives the smallest moment area of bridge for the moving and impact loads does not apply to the moment area of the dead load. In very long spans the dead loads are most important and the moment areas of the dead load are smaller for longer cantilever arms.

To find the best length of the suspended span, the weight of the bridge for several lengths of the suspended span should be calculated by the formula hereafter given, and the length which gives, considering the cost of erection, the cheapest bridge should be chosen, unless æsthetic considerations govern.

For

$$l_c = l_s = \frac{L}{3}$$
 and  $l_a = \frac{5}{6}l_c = \frac{5}{18}L$ 

we obtain for the moment area of the bridge for a unit moving load per lineal foot  $M_b^a = 0.778 \frac{L^3}{L^2}$ 

For the corresponding shear area we find

$$S_b^a = 1.521 \cdot \frac{L^2}{3}$$

The anchorage tension is

$$S_a^{end} = \frac{2}{5}L$$

For the main span the moment area is

$$M_L^a = \frac{11}{27} \frac{L^3}{12}$$

The shear area is

$$S_L^a = 0.778 \frac{L^2}{3}$$

For the same three ordinary independent truss spans the moment and shear areas from unit load per foot are:

$$M_{B_i}^a = 1.043 \frac{L^3}{12}$$

$$S_{Bi}^{a} = 1.1543 \frac{L^{2}}{3}$$

A comparison of the moment and shear areas of the three spans built as a cantilever with those when built as independent spans shows that for the moving load stresses a cantilever bridge offers no apparent advantage over independent spans. For short spans, where the moving load stresses are most important, independent spans are equally economical.

For certain situations, where a scaffolding is expensive or impossible, the easier erection of the main span of a cantilever bridge

will give it decided advantage.

In long spans the dead load stresses are the most important, and of these those from the dead loads of the main span. In a bridge of three independent spans the dead loads are nearly uniformly distributed over each span. In a cantilever bridge of three spans the dead loads are mainly near the two piers carrying the main span. The moment and shear areas from dead loads are, therefore, very much smaller than those from an equal amount of uniformly distributed load. This advantage is of increasing importance with increase in the length of the main span.

Independent spans of more than 700 feet are, therefore, seldom

advisable.

Definite information on these subjects is best obtained by means of formulas for the weight of steel in a cantilever bridge as a function of the load, the general dimensions, and the unit stresses.

The suspended span is an independent span for which the formulas have been already given. For the cantilever arms we have:

Weight of steel of one cantilever arm with parallel chords:

$$W_{p}^{c} = W_{\mu} + W_{\mu}^{d_{1}} + W_{\mu}^{d_{2}} + W_{\mu}^{d_{3}} + W_{\omega} + W_{\omega}^{d_{1}} + W_{\omega}^{d_{2}} + F + W_{f}^{d_{1}} + W_{f}^{d_{2}} + R.$$

$$(45)$$

In this formula:

 $W_{p}^{c}$  = weight of steel in one cantilever arm with parallel chords

$$W_{\mu} = \frac{\mu l_c}{12} \left\{ A l_c \left( 2 l_c + 3 l_s \right) + 6 B \left( l_c + l_s \right) \right\} \quad \cdots \quad (46)$$

 $W_{\mu}$ = weight of steel in the cantilever trusses required for the moving load and impact stresses.

 $\mu$  = uniform load per lineal foot, giving the same weight of truss as the moving load  $m_r + m_h$  with the impact of  $m_r$ .

 $m_r$  is approximately the uniform moving load giving the same moment at the distance  $-\frac{2}{3}l_c$  from the end of the cantilever arm as the actual railway load.

$$\mu = m_r (\mathbf{1} + I) + m_h \dots \tag{47}$$

$$I = \frac{300}{300 + l_s + l_c}$$
 for single track.....(48)

$$I = \frac{300}{300 + 2 (l_s + l_c)}$$
 for double track.....(49)

 $l_c = length of cantilever arm$ 

 $l_s = \text{length of suspended span.}$ 

For A and B see equations (4), (12), (13), and (14).

$$W_{\mu}^{d_{1}} = \frac{\mu V l_{c}}{240} \left[ A l_{c}^{2} \left\{ A l_{c} \left( 2 l_{c} + 5 l_{s} \right) + 20 B \left( l_{c} + 2 l_{s} \right) \right\} + 20 B^{2} l_{c} \left( 2 l_{c} + 3 l_{s} \right) + \frac{60 W_{s}}{\mu} \left( A l_{c} + 2 B \right) \right] \dots$$
 (50)

 $W^{d_1}_{\mu}=$  weight of steel in the cantilever trusses required to carry  $W_{\mu}$  and  $W_{s}$ 

$$V \sim 0.97$$

 $W_s$  = Total weight of suspended span.

$$W_{\mu}^{d_{2}} = \frac{\mu V^{2} l_{c}^{3}}{240} \left[ \frac{A^{3} l_{c}^{3}}{42} \left( 2l_{c} + 7l_{s} \right) + A^{2} B l_{c}^{2} \left( l_{c} + 3l_{s} \right) + 3 A B^{2} l_{c} \left( 2l_{c} + 5l_{s} \right) + 10 B^{3} \left( l_{c} + 2l_{s} \right) + \frac{5 W_{s}}{\mu l_{c}} \cdot \left( A^{2} l_{c}^{2} + 8 A B l_{c} + 12 B^{2} \right) \right] .$$
 (51)

 $W^{d_2}_{\mu}=$  weight of steel in the cantilever trusses required to carry  $W^{d_1}_{\mu}$ 

$$W_{\mu}^{d_3} = \frac{\mu V^3 l_c^4}{240 \times 168} \left[ \frac{A^4 l_c^4}{18} \left( 2l_c + 9l_s \right) + 4A^3 B l_c^3 \left( l_c + 4l_s \right) \right]$$

$$+ 24 A^{2} B^{2} l_{c}^{2} (2l_{c} + 7l_{c}) + 224 AB^{3} l_{c} (l_{c} + 3l_{s})$$

$$+ 168 B^{4} (2l_{c} + 5l_{s}) + \frac{28 W_{s}}{\mu l_{c}} \left\{ A^{2} l_{c}^{2} (Al_{c} + 18B) + 30B^{2} (3Al_{c} + 4B) \right\}$$

$$- (52)$$

 $W_{\mu}^{d_3}=$  weight of steel in the cantilever trusses required to carry  $W_{\mu}^{d_2}$ 

$$W_{\omega} = \frac{6.8 \, \alpha_c \, l_c^2}{24 \, B_r \, U_c} \left\{ 6 p_{ws} \, l_s + l_c \, (4a + bl_c) \right\} + \frac{3.4 \, \alpha_l \, l_c}{U_l \, \sin \, 2\beta l} \left\{ 3 p_{ws} \, l_s + l_c \, (3a + bl_c) \right\} \dots$$
 (53)

 $W\omega$  = weight of steel in the laterals and cross bracing of one cantilever arm. This includes the steel in the chords of the main trusses to resist the wind stresses in them.

 $B_r$  = breadth or width of bridge.

 $p_{ws} = p_w$  of suspended span given in the equations (32) to (37).

 $\alpha$  = wind pressure per lineal foot of bridge at end of cantilever arm

$$a \sim p_{ws}$$
  $b \sim 1$ 

 $p_{wc} = a + bx = \text{wind pressure per foot of cantilever arms at the distance } x \text{ from its end.}$ 

 $\alpha_l = 2.6$  for carbon steel,  $\alpha_l = 3.0$  for nickel steel, both with lateral and cross bracing diagonal struts made of four or eight angles latticed on four sides.

 $a_c = 1.45$  when full compression splices and lacing able to resist a cross shear = 2 per cent. of the axial stress is prescribed.

 $\beta_l$  = angle of the laterals with the cross struts.

 $U_l$  = axial unit stress in the laterals.

 $U_c$  = axial unit stress in the bottom chords of the trusses of the cantilever arm.

Vol. CLXXVI, No. 1056-47

$$\begin{split} W_{\omega}^{d_{1}} &= \frac{VCl_{c}^{3}}{360} \left[ Al_{c} \left\{ 15E + l_{c} \left( 6 \ a + bl_{c} \right) + 6B \left\{ 10E + l_{c} \left( 5a + bl_{c} \right) \right\} \right] \\ &+ \frac{VDl_{c}^{2}}{20} \left[ Al_{c} \left\{ 10E + l_{c} \left( 5a + bl_{c} \right) \right\} + 5B \left\{ 6E + l_{c} \left( 4a + bl_{c} \right) \right\} \right]. (54) \end{split}$$

 $W^{d_1}_{\omega}=$  weight of steel in the cantilever trusses required to carry  $W_{\omega}$ 

$$C = \frac{3 \cdot 4 \, \alpha_c}{B_r \, U_c} \, \dots \, (55)$$

$$D = \frac{3 \cdot 4 \, \alpha_l}{U_l \sin \, 2\beta_l} \tag{56}$$

$$E = p_{\omega s} l_s. \tag{57}$$

$$\begin{split} W_{\omega}^{d_2} &= \frac{V^2 l_c{}^3}{720} \Big[ A^2 l_c{}^2 \left[ C l_c \left\{ E + \frac{l_c}{28} \left( 8a + b l_c \right) \right. \right] \\ &+ 6D \left\{ 3E + \frac{l_c}{7} \left( 7a + b l_c \right) \right\} \Big] \\ &+ 4AB l_c \left[ C l_c \left\{ 3E + \frac{l_c}{7} \left( 7a + b l_c \right) \right. \right] \\ &+ 3D \left\{ 15E + l_c \left( 6a + b l_c \right) \right\} \Big] \\ &+ 2B^2 \left[ C l_c \left\{ 15E + l_c \left( 6a + b l_c \right) \right\} \right] \\ &+ 18D \left\{ 10E + l_c \left( 5a + b l_c \right) \right\} \Big] \Big] \end{split}$$

 $W^{d_2}_{\omega}=$  weight of steel in the cantilever trusses required to carry  $W^{d_1}_{\omega}$ 

F is the weight of steel in the floor of the cantilever arm.

$$W_f^{d_1} = \frac{Vfl_c^2}{6} (Al_c + 3B) \dots (59)$$

 $W_f^{d_1}$  = weight of steel in the cantilever trusses required to carry the floor of the cantilever arm.

f = total weight of floor of the cantilever arm per lineal foot of its length (includes timber, snow, etc.).

$$W_f^{d_2} = \frac{V^2 f_c^{13}}{120} \left[ A l_c \left( A l_c + 10B \right) + 20B^2 \right] \dots$$
 (60)

 $W_f^{d_2}=$  Weight of steel in the cantilever trusses required to carry  $\mathbf{W}_f^{d_1}$ .

The coefficient V varies slightly with different engines and different specifications regarding the position of the engines in the train and with the web systems  $V \sim 0.97$ .

R = a rest to cover the weight of steel in the cantilever trusses required to carry

$$W^{d_3}_{\mu} + W^{d_2}_{\omega} + W^{d_2}_{f} + R$$

The succeeding  $W^d_\mu$   $W^d_\omega$  and  $W^d_f$  decrease in size. From the rate of decrease the member of each series following the last one given can be roughly estimated and the value R thereby approximately determined.

R is always small.

$$a_c = 1.45.$$

For eyebars,  $\alpha_t = 1.25 = \alpha_{t_1}$ 

This value of  $\alpha_c$  assumes that the specification prescribes full splices in compression members and lacing able to carry a cross load equal to 2 per cent. of their axial stress.

The above formulas (45) to (60) are good for all values of  $l_s$  and  $l_c$ .

For  $l_s = l_c = \frac{L}{3}$  the formulas are as follows:

$$W_{\mu} = \frac{\iota \iota l_c^2}{12} \left\{ 5Al_c + 12B \right\}$$
 (46a)

$$W_{\mu}^{d_{1}} = \frac{\mu V l_{c}^{3}}{240} \left\{ A l_{c} \left( 7A l_{c} + 60B \right) + 100B^{2} + \frac{60W_{s}}{\mu l_{c}^{2}} (A l_{c} + 2B) \right\} (50a)$$

$$W_{\mu}^{d_2} = \frac{\mu V^2 l_c^4}{240} \left[ \frac{A^2 l_c^2}{14} \left( 3A l_c + 56B \right) + 3B^2 \left( 7A l_c + 10B \right) + \frac{5W_s}{\mu l_c^2} \left( A^2 l_c^2 + 8AB l_c + 12B^2 \right) \right] \cdot (51a)$$

$$W_{\mu}^{d_{3}} = \frac{\mu V^{3} l_{c}^{5}}{240 \times 168} \left[ A^{2} l_{c}^{2} \left( \frac{11}{18} A^{2} l_{c}^{2} + 20AB l_{c} + 216B^{2} \right) + 56B^{3} \left( 16A l_{c} + 21B \right) + \frac{28W_{s}}{\mu l_{c}^{2}} \left\{ A^{2} l_{c}^{2} \left( A l_{c} + 18B \right) + 30B^{2} \left( 3A l_{c} + 4B \right) \right\} \right] ......(52a)$$

(53a) to (60a) are identical with (53) to (60).

#### CANTILEVER ARMS WITH INCLINED CHORDS.

To obtain simple formulas for the weight of such cantilevers we find first the formula for the weight of a cantilever truss with inclined chords carrying a uniform load per lineal foot, then that when carrying a load which increases uniformly from the end to the main pier. We then compare these weights for inclined chords with those for parallel chords, and we find that the weights of the cantilever with inclined chords can be obtained by finding the weights with parallel chords and multiplying them with coefficients given below.

$$W_{i}^{c} = 0.81 W_{\mu} + W_{\omega}^{I} + F + 0.81 \left\{ 0.81 W_{\mu_{1}}^{d_{1}} + W_{s}^{d_{1}} + W_{\omega}^{Id_{1}} + W_{\sigma}^{Id_{1}} + W_{f}^{Id_{1}} \right\} + 0.81^{2} \left\{ 0.81 W_{\mu_{1}}^{d_{2}} + W_{s}^{d_{2}} + W_{\omega}^{Id_{2}} + W_{f}^{Id_{2}} \right\} + 0.81^{3} \left\{ 0.81 W_{\mu_{1}}^{d_{3}} + W_{s}^{d_{3}} \right\} + R \dots$$
(61)

Where  $W^{\rm I}_{\omega}W^{{\rm I}d_1}_{\omega}$  and  $W^{{\rm I}d_2}_{\omega}$  are found by taking for  $l_c-l_c\sec\delta_c$  in formulas (53) to (58)

$$W_{\mu_1}^{d_1} = \frac{\mu V l_c^2}{240} \left[ A l_c \left\{ A l_c \left( 2 l_c + 5 l_s \right) + 20B \left( l_c + 2 l_s \right) \right\} + 20B^2 \right]$$

$$\left( 2 l_c + 3 l_s \right)$$

$$(50 b)$$

$$W_s^{d_1} = \frac{V l_c W_s}{4} \left( A l_c + 2B \right) \dots$$
 (50 c)

$$W_{\mu^{1}}^{d_{2}} = \frac{\mu V^{2} l_{c}^{3}}{240} \left[ \frac{A^{3} l_{c}^{3}}{42} \left( 2l_{c} + 7l_{s} \right) + A^{2} B l_{c}^{2} \left( l_{c} + 3l_{s} \right) + 3AB^{2} l_{c} + (2l_{c} + 5l_{s}) + 10B^{2} \left( l_{c} + 2l_{s} \right) \right] \dots (51 \text{ b})$$

$$W_{s}^{d_{2}} = \frac{V^{2}l_{c}^{2}W_{s}}{48} \left( A^{2}l_{c}^{2} + 8ABl_{c} + 12B^{2} \right)$$

$$W_{\mu_{1}}^{d_{3}} = \frac{\mu V^{3}l_{c}^{4}}{240 + 168} \left[ \frac{A^{4}l_{c}^{4}}{18} \left( 2l_{c} + 9l_{s} \right) + 4A^{3}Bl_{c}^{3} \left( l_{c} + 4l_{s} \right) + 24A^{2}B^{2}l_{c}^{2} \left( 2l_{c} + 7l_{s} \right) + 224AB^{3}l_{c} \left( l_{c} + 3l_{s} \right) + 168B^{4} \left( 2l_{c} + 5l_{s} \right) \right] \dots (52b)$$

$$W_s^{d_3} = \frac{V^3 l_c^3 W_s}{1440} \left\{ A^2 l_c^2 \left( A l_c + 18B \right) + 30B^2 \left( 3A l_c + 4B \right) \right\}$$
 (52 c)

 $W_i^c$  = weight of cantilever arm with inclined chords when  $l_s$  and  $l_c$  are nearly alike and when the height at end is

$$h_e = \frac{h_p}{4.5} = \frac{l_c}{9}$$

 $h_p$  = height at main pier. These heights  $h_p$  and  $h_c$  are approximately the most economical heights for very long spans with independent erection of the suspended span and floating into position.

The suspended span will, in this case, be built with curved top or bottom chord.

A subdivided K system of web members is for the cantilever arms of very long main spans of 1200 to 1800 feet the most economical web system, and was here assumed.

 $W_i^c$  includes that part of the vertical posts above the main pier which is required for the loads coming from the cantilever arm, and it includes one-half of the cross bracing between these posts.

The height h which must be used for the calculation of A, B, and  $\beta$  is 0.344  $l_c = 0.688 h_b$ .

The cantilever arm with parallel chords, which is here used as a substitute for the actual arm with inclined chords, has equal panels.

The actual cantilever arm with inclined chords for a bridge with independent erection of the suspended span is for very long main spans of 1000 to 1800 feet best designed with panels increasing in length from the end to the main pier so as to obtain more nearly equal angles  $\beta$  for the diagonals. Panels 60 per cent. longer at the main pier than at the end of the cantilever arm are economical. The best average panel length for very long spans double track is

$$_{27} + \frac{4L}{300}$$
 feet.

When the suspended span is erected by building out from the ends of the two cantilever arms it is best built with parallel chords and equal panels.

The cantilever arms have then less variation in height, and equal panels can be used without very much increase in weight.

The cost of erection is materially reduced by uniform panel length.

Formula (61) does not apply to a cantilever arm with this larger height at end. The coefficients are here different and are found in a similar manner as for a cantilever arm with smaller end height.

The formula for the weight of steel of a cantilever arm with

$$h_c = \frac{\text{I.I}L}{18}$$
 and  $h_p = \frac{L}{6}$ 

with a K system of web members and with equal panels of the most economical length is given below.

The formula is approximately correct also with other web systems and  $h_p = 0.15L$  with proper choice of B.

For very long spans  $l_s = l_c$ ; for shorter spans  $l_c$  is slightly smaller than  $l_s$ .

### FURTHER EXPERIMENTS ON BISMUTH THER-MOPILES.\*

# BY WM. W. COBLENTZ, Ph.D.,

Associate Physicist, U. S. Bureau of Standards.

The bismuth-silver thermopile appears to be winning a favorable place among the numerous devices employed in measuring radiant energy. The object of the present note is to describe experimental tests illustrating the shortcomings of some of the theoretical deductions relative to the construction of thermopiles.

I. Relation between External and Internal Resistance.—The older theories held that the maximum efficiency is attained when the external (the galvanometer) resistance is the same as the (internal) resistance of the thermopile. During recent years, however, Altenkirch 1 came to the conclusion, theoretically, that the external resistance can be two to three times the internal resistance of the pile, without seriously affecting its maximum efficiency. It therefore seemed desirable to subject the question to experimental test. In a previous paper 2 it was found, when the three units of a large surface thermopile were connected in series, thus producing an internal resistance which was about 6.4 times the external (galvanometer) resistance, that the radiation sensitivity was about two-thirds that of the thermopile having the units joined in parallel and having practically the same resistance as that of the galvanometer.

In the recent experiments the external resistance was greater than the internal resistance. In one outfit consisting of a galvanometer having four coils of 21 ohms resistance, and a thermopile having a resistance of 9.7 ohms, the radiation sensitivity was the same when the coils were in series-parallel (21 ohms) or all in parallel (5.3 ohms). The test was, of course, not very crucial, for it showed simply that when the external resistance was twice as great, or only half as great as the internal resistance,

<sup>\*</sup> Communicated by the author.

<sup>&</sup>lt;sup>1</sup> Altenkirch, Phys. Zeitschr., 10, p. 560 (1909).

<sup>&</sup>lt;sup>2</sup> Coblentz, Bull. Bur. Standards 9, p. 7 (1912).

the sensitivity was the same. The crucial test was made with a galvanometer consisting of 26-ohm coils mounted in the soft iron shields previously described.<sup>3</sup> This magnetic shield was sufficient to eliminate the ordinary magnetic disturbances and at the same time easily permitted the joining of the coils in various combinations: (1) all in series, (2) all in parallel, (3) two in series-parallel, giving 104, 6.5, and 26 ohms respectively. The thermopile was exposed to a standard of radiation <sup>4</sup> consisting of a seasoned incandescent lamp calibrated against a black body. Using a thermopile, having a resistance of 13.9 ohms, and an external resistance of 104 ohms, the radiation sensitivity was 31 per cent. less than when the external resistance was 26 ohms,—i.e., the galvanometer resistance was respectively eight and two times that of the thermopile.

The most important test was with a thermopile having a resistance of 6.8 ohms. When the external resistance was four times (i.e., 26 ohms) that of the thermopile the radiation sensitivity was 16.4 to 17 per cent. less than when the external resistance (6.5 ohms) was the same as the internal (thermopile) resistance. In view of the fact that there was a loss of only 16.5 per cent. in efficiency when the external resistance was four times the internal resistance, and in view of the fact that one rarely meets with conditions where the galvanometer resistance is more than twice the resistance of the thermopile, it is evident that this question proves to be of minor importance. Nevertheless, it was important to settle the question, for one of the first specifications of intending purchasers of these instruments is that the resistances of the two instruments must be equal.

2. The Radiation Sensitivity of a Thermopile.—The factors which determine the radiation sensitivity of a vacuum thermopile, as enunciated by Johansen,<sup>5</sup> are as follows: (1) The resistance of the thermopile should be equal to that of the galvanometer; (2) the radii of the two wires of the element should be so chosen that the ratio between the heat conductivity and the electrical resistance is the same in both; (3) the heat loss by conduction through the wires should be equal to the heat loss by radiation

<sup>&</sup>lt;sup>8</sup> Coblentz, Bull. Bur. Standards 9, p. 7 (1912) (see Fig. 17).

<sup>4&</sup>quot; A Secondary Standard of Radiation," Jour. Franklin Institute, 176, p. 219 (1913).

<sup>&</sup>lt;sup>5</sup> Johansen, Ann. der Phys. (4), 33, p. 517 (1910).

from the junctions; (4) the radiation sensitivity is proportional to the square root of the exposed surface.

In previous papers <sup>6</sup> it was shown experimentally that rules (2) and (4) are only approximately true. In fact, the best diameter of silver wire (0.036 to 0.038 mm.) to be used with a 0.1 bismuth wire was found without considering the theory. In the same manner an iron wire 0.0308 mm. diameter was found better than one 0.0418 mm. in diameter, although theory would have required the thicker wire.

Rule (3) tells us nothing but what must be obtained by experiment, and that must be obtained on a complete thermopile. For example, one would naturally try to use flat bismuth wire to avoid heat conduction. The test, using a single pair of junctions, showed <sup>7</sup> that the flat wire gave a radiation sensitivity which was about 9 per cent. higher than that of a junction made of round wire. A thermopile was therefore constructed with the greatest care. It embodied the experience and improvements resulting from the construction of 21 thermopiles. It contained 28 elements; had an area of 2 by 14.5 mm. and a resistance of 13.5 ohms. It proved to be the quickest acting of all the instruments yet constructed, but its intrinsic radiation sensitivity (i.e., sensitivity per mm.<sup>2</sup> of exposed surface) was only 16.4, when all the others, similarly constructed, of round wires had a radiation sensitivity of 25.5 to 26.

The results showed that in smoking the thermopile the flat wires were given a different relation between the emissivity and conductivity than obtained in the round bismuth wires. Johansen's rule (3) was not fulfilled; and nothing but a prolonged experiment sufficed to determine the best mode of construction. The bismuth-silver thermopile is based upon experiment. Its novelty is the completely opaque receiver, while at the same time maintaining a symmetry of the hot and the cold junctions as found in the Rubens and older types of thermopiles.

<sup>&</sup>lt;sup>6</sup> Coblentz: Bull. Bur. Standards 9, p. 7 (1912). JOURNAL FRANKLIN INSTITUTE, 175, p. 497 (1913). Physikalische Zeitschr., xiv, 683 (1913). Jour. Wash. Acad. Sci., 3, p. 357 (1913). These experiments were made on thermopiles in air. There is a distinct field of investigations requiring thermopiles in air.

<sup>&</sup>lt;sup>7</sup> Coblentz: Phys. Zeitschr., xiv, 683 (1913). Jour. Wash. Accd. Sci., 3, p. 357 (1913).

In some forms of thermopiles now being put on the market the cold junctions are attached to the metal supporters. This introduces a dissymmetry between the hot and cold junctions, and hence a likelihood of "drift" of the galvanometer needles. For the incident radiation warms the surrounding air, and the cold junctions, because of their greater heat capacity, cannot quickly take the temperature of the surroundings.

By making the small receivers twice as long and attaching two junctions to each receiver, less shellac is required for insulation between the hot junctions, and the heat capacity, the emissivity, and the resistance are reduced. A thermopile built on this principle, consisting of nine pairs of junctions joined in series-parallel, had a resistance of 2.2 ohms. If the 18 elements had been joined in series the resistance would have been four times as great. In this thermopile the receivers were 2 by 2.1 mm., making a completely opaque curtain 2 by 18.5 mm. in area. The device is more sensitive and quicker acting than the old style, and it was entirely free from drift.

The receivers are made of platinum, which remains bright on the rear, unprotected side, thus keeping a low emissivity. Silver receivers might be better when new, but eventually the rear (unprotected) side would become black, thus increasing the emissivity. The use of thin metallic receivers permits a modification of the device to suit the individual problem. For example, in a physiological problem involving the question of the heat produced in a stimulated nerve the receiver is built in the form of a long, U-shaped trough, 21.5 mm, in length, within and along the axis of which is suspended the sample under investigation. This thermopile receives heat by radiation and by conduction from the material placed within the U-shaped receiver. The sensitivity (approximate value) was tested by placing a silk-covered manganin wire (0.05 mm. diameter, resistance 4.5 ohms) within the receiver, and passing an electric current through it. Using a galvanometer sensitivity of 5 × 10-10 ampère, a deflection of I mm. =  $4.3 \times 10^{-8}$  watt, or  $1 \times 10^{-8}$  calorie was shown.

It is desirable to emphasize the importance of examining the electromotive force of the bismuth wire. Of the eight samples tested (diameters 0.06, 0.08, 0.1, and 0.15 mm.), the thermoelectric power, against silver, varied from 75 to 82 microvolts. This seems to depend upon the purity of the material, as indicated

by the purchases at different times. The material received in one order of 0.08 and 0.1 mm. bismuth wire gave 76 microvolts, while another order consisted of material giving 75 and 82 microvolts respectively.

The electromotive forces of various thermopiles, exposed to a standard of radiation, was measured with an ordinary potentiometer. The actual voltages developed varied from 6 to 20 microvolts (depending, of course, upon the number of thermojunctions, and especially upon the area exposed), which was equivalent to 0.20 to 0.25 microvolt per microwatt. One thermopile gave 0.35 microvolt per microwatt. The *efficiency* per single junction, in the thermopiles examined, varied from 0.011 to 0.014 microvolt per microwatt of radiant energy. Since the thermoelectric power is about 78 microvolts, the results show that 1 microwatt produces a rise in temperature of about 15° x 10<sup>-5</sup> C. above the surrounding air. This seems the most logical way to rate the efficiency of a thermopile.

In most of the thermopiles there was but little gain by placing more than one thermojunction per 0.8 mm. length of the complete receiver, and ordinarily it would be sufficient to place them at a distance of 1.2 mm. length. This should be sufficient to give a correct integration of the incident radiation if it should not be uniformly distributed.

Recent investigations's show that an alloy of Bi + 9 per cent. Sb gives a higher electromotive force than pure bismuth; but this alloy is too brittle for thermopiles. The best combination which gives fine annealed threads, by spattering, is Bi + 4 per cent, antimony. The electromotive force of the material must be tested, however, for some samples give a lower electromotive force than the best wire of pure bismuth.

An alloy of Bi + 5 to 6 per cent. tin gives 44 to 45 microvolts. When used with the best bismuth wire the thermal element

<sup>8</sup> Haken: Ann. der Phys. (4), 32, p. 291 (1910).

Gelhoff and Newmeier: Verh. Phys. Gesell., 15, p. 876 (1913).

<sup>&</sup>lt;sup>9</sup> Coblentz: Bull. Bur. Standards 7, p. 248 (1910). This method, which seemed too ridiculous for description at that time, is one of the chief contributions to the improvement of thermopiles. By dropping the molten metal from a height, upon an inclined glass plate, the metal is drawn out into thin, well-annealed threads. Pfund (Phys. Rev., 34, p. 228, 1912) goes a step further, and hurls the molten metal against the glass plate. This produces longer threads, of great uniformity.

gives an electromotive force of 126 to 128 microvolts. An element consisting of pure bismuth wire and an alloy of Sb, Cd, Bi gave 138 to 140 microvolts per degree; but the alloy is too brittle for an ordinary thermopile. The most promising thermopile appears to be one having elements of pure bismuth and an alloy of Bi + 6 per cent. tin, joined in series-parallel, as already described.

In conclusion it may be added that in the discussion of theory versus experiment it is not intended to detract from the theoretical contribution to the subject. On the other hand, it is but fair to emphasize the contributions which had to be worked out experimentally. These experiments relate to the most crucial points in thermopile construction, especially the question of heat conduction and emissivity, upon which theory could be of little assistance.

Washington, D. C., October 25, 1913.

Natural Gaseous Mixtures Rich in Helium. C. Moureu and A. Lepape. (Compt. Rend., clv, 197.)—The following mineral springs evolve gas containing a large percentage of helium. The natural gas from the springs at Sautenay contains from 8.4 to 10.1 per cent. of helium, that from springs at Maiziéres contains 5.9 per cent.; from springs at Grisy, 2.18 per cent.; from Bourbon Lancy, 1.84 per cent.; from Néris, 0.97 per cent.; and from La Bourboule, only 0.1 per cent. The quantities are too large to be considered as nascent helium evolved immediately it is produced; and it is more probable that the immediate source is dissolved helium, evolved by the disintegration of minerals in which it has been absorbed. These sources are grouped in the neighborhood of Moulins, Dijon, and Vesoul.

Pressure-Balanced Piston Rings. Anon. (Eng., cxv, 521.)—
This paper describes piston rings by Allen and Simmons, Ltd., which are designed to decrease the friction of piston rings and, consequently, the lost power. The fundamental idea is to balance the outward radial pressure of steam behind the rings by giving them a suitable cross section. It is shown by calculation that, whereas the frictional losses caused by Ramsbottom rings might be 4.8 per cent., the loss with the Allen rings is only 0.173 per cent. The same idea is applied to piston valves, air-pump buckets, and gland packing. It is also shown that it is possible, by the use of Allen rings, to employ a very simple form of piston, which is cheaper to construct and is more efficient thermally than the ordinary type.

## EVIDENCE BEARING ON THE SOLVATE THEORY OF SOLUTION.\*

BY

### HARRY C. JONES.

[The investigations referred to in this paper have been largely carried out with the aid of grants from the Carnegie Institution of Washington.

This paper has been written in response to a request from the Editor of the JOURNAL OF THE FRANKLIN INSTITUTE, to summarize for this journal the experimental evidence obtained in my laboratory, bearing upon the solvate theory of solution as it originated here about fourteen years ago.]

In the following tables, under  $\lambda$  are given the wave-lengths of light that were passed through the solution, and under  $I/I_0$  the percentage of transmission, on the one hand, of the solution, and, on the other, of water having a depth exactly equal to that of the water in the solution.

The ordinates of the curve, as has already been stated, are percentage transmissions and the abscissæ wave-lengths.

			TABLE I.			
	KC1		NH4Cl		NH4NO3	
	$_{I/I_{o}}^{4 \text{ N}}$	H <sub>2</sub> O	4 N I/I <sub>0</sub>	$_{\mathrm{H_2O}}$	3.12 N I/I <sub>0</sub>	$_{\mathrm{H_2O}}$
710	97	97	92	98	95	98
724	96	95	91	96	97	98
741	95	95	90	92	96	96
760	93	95	85	92	91	95
776	92	95	85	88	92	94
798	94	95	88	95	91	95
818	92	95	87	95	92	96
836	94	93	87	95	91	94
855	91	90	86	93	89	92
878	92	90	86	91	90	93
900	90	89	84	87	89	88
922	87	86	82	86	85	90
947	82	84	79	82	82	83
958	77	78	73	72	73	79
964	75	73	69	70	70	71
969	65	65	64	63	65	67
974	58	56	57	58 -	58	59
979	51	50	52	52	50	54
982	47	46	45	46	44	46
985	41	45	43	43	40	44
991	39	43	41	43	39	43

<sup>\*</sup> Concluded from page 564.

	KC1		NH <sub>4</sub> C1 4 N		NH <sub>4</sub> NO <sub>3</sub> 3.12 N	
	4 N I/I <sub>o</sub>	$H_2O$	$I/I_{o}$	$H_2O$	$I/I_{\rm o}$	$H_2O$
1007	39	43	41	42	39	44
1013	40	42	39	44	41	44
1019	42	46	40	46	42	44
1025	41	42	44	49	45	48
1032	49	49	44	49	48	49
1037	53	52	56	55	52	53
1042	56	56	53	58	55	55
1046	59	60	57	57	57	60
1059	63	62	58	65	60	65
1065	68	67	62	67	64	65
1072	71	68	64	68	66	69
1078	74	72	67	67	66	72
1085	75	73	67	66	68	74
1100	77	75	68	72	69	78
1113	76	76	69	72	69	78
1138	75	72	68	70	68	72
1148	70	69	64	-65	64	71
1158	64	63	62	64	59	64
1165	58	59	58	58	56	60
1172	52	51	50	50	53	52
1179	42	40	40	40	38	41
1186	29	28	29	26	29	30
1193	18	19	19	19	18	19
1200	13	16	14	13	12	17
1206	10	12	12	12	9	13
1213	10	ΙΙ	10	12	9	13
1220	IO	ΙΙ	10	ΙΙ	9	12
1227	10	ΙΙ	10	II	9	12

In the above table the depth of layer of all the solutions was the difference between 21 and 1,—i.e., 20 mm. The depth of water was in every case the same as that of the water in the solution in question.

The depth of layer of the following solutions was the difference between 11 mm. and 1 mm.,—i.e., 10 mm. The depth of water used was in every case the same as that of the water in the solution:

			TABLE II.			
	KC1 4 N I/I <sub>0</sub>	$_{ m H_2O}$	NH <sub>4</sub> C1 4 N I/I <sub>0</sub>	H <sub>2</sub> O	NH <sub>4</sub> NO <sub>3</sub> 3.12 N I/I <sub>0</sub>	H₂O
1085	85	86	79	87	81	88
1100	87	88	80	92	81	93
1113	86	87	79	86	84	86
1138	81	85	79	8.1	81	84

	KC1		NH <sub>4</sub> Cl		NH4NO3	
	4 N I I.	$_{\mathrm{H_2O}}$	4 N I I I o	H <sub>2</sub> O	3.12 N I/I <sub>0</sub>	$H_2O$
1148	79	82	77	84	78	84
1158	80	79	74	81	76	81
1165	76	77	71	77	72	77
1172	72	71	66	70	67	70
1179	64	62	59	62	61	62
1186	51	51	52	50	50	50
1193	41	43	42	44	40	44
1200	35	38	37	40	34	40
1206	37	36	35	37	32	37
1213	30	34	30	36	32	36
1220	30	35	29	35	34	35
1227	30	34	30	35	32	35
1233	30	33	28	35	31	35
1241	30	34	29	34	31	34
1248	31	34	28	33	31	33
1250	33	34	30	34	32	34
1255	34	35	30	36	32	36
1268	34	35	31	37	32	37
1270	37	31	32	38	33	38
1285	38	38	33	38	33	38
1295	39	38	32	38	33	38
1300	41	38	32	39	34	39
1308	42	39	32	41	35	41
1316	41	39	32	40	34	40
1323	42	37	32	38	34	38
1330	40	37	32	37	33	37
1338	40	35	30	35	31	35
1346	36	33	28	36	30	36
1352	34	29	26	29	27	29
1358	29	26	23	27	25	27
1365	25	22	21	23	21	23
1372	20	18	17	20	17	20
1387	13	12	12	II	IQ	II
1404	7	7	7	8	7	8
1418	3	4	4	3	3	3
1430	2	2	3	2	2	2
1445	0	0	0	I	I	I

In Table II the depth of layer of the solution that was used was only half of that in Table I. The object of this was to bring out more prominently the second water-band.

The depth of layer of the following solutions was the difference between 21 mm. and 1 mm.,—i.e., 20 mm. The depth of water used in every case was the same as that of the water in the solution:

TABLE III.

	CaCl <sub>2</sub> 5 · 38 N I/I <sub>0</sub>	H <sub>2</sub> O	MgCl <sub>2</sub> 4.96 N I/I <sub>0</sub>	H <sub>2</sub> O	Al <sub>2</sub> (SO <sub>4</sub> ) <sup>2</sup> 1.02 N I/I <sub>0</sub>	H <sub>2</sub> O
710	94	98	95	98	95	93
724	94	98	98	98	95	95
74I	92	95	95	98	94	93
760	87	93 94	93 94	98	92	93
776	88	93	94	97	93	95 95
798	91	93 96	93	97	93 92	90
798 818			93 90	94	-	90
836	93	99	-	_	93 92	92
_	92	97	92	95	-	92 91
855	90	93	91	90	90 91	90
878	90	90	91 88	93	89	
900	89	92	88	92	85	90 86
922	86	91		9 <b>I</b>		
947	87	84	84	86	82	81
958	78	79	76	78	76	73
964	75	73	82	76	72	66
969	70	68	75	69	68	61
974	65	62	68	65	64	55
979	59	53	61	56	58	48
982	51	49	48	51	53	42
985	48	49	54	45	51	40
991	44	46	48	49	47	39
1007	42	46	46	48	46	38
1013	42	46	45	50	46	39
1019	43	49	44	51	44	40
1025	47	50	46	44	46	43
1032	52	53	51	54	46	45
1037	55	55	52	56	52	50
1042	58	59	56	58	53	53
1046	62	62	59	65	55	55
1059	66	65	63	67	55	58
1065	71	70	69	70	62	63
1072	74	72	71	75	60	65
1078	75	74	71	76	64	69
1085	78	76	<del>7</del> 6	79	65	70
1100	80	77	78	79	67	72
1113	79	78	8o	81	67	74
1138	77	75	77	78	64	67
1148	74	71	75	77	60	65
1158	69	65	73	73	57	55
1165	66	62	65	65	55	53
1172	61	52	61	58	50	43
1172	54	52 41	52	44	45	34
11/9		30	43	32	34	22
	42	21	43 32	24	25	15
1193	32	21	32	*4	~3	13

	CaCl <sub>2</sub> 5 · 38 N I / I <sub>o</sub>	H <sub>2</sub> O	MgCl <sub>2</sub> 4.96 N I/I <sub>0</sub>	H <sub>2</sub> O	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> I.O2 N I/I <sub>0</sub>	H <sub>2</sub> O
1200	22	17	23	18	20	12
1206	16	16	18	17	16	10
1213	13	15	16	18	14	9
1220	12	13	14	15	II	10
1227	12	13	14	16	12	8

In the following table the depth of layer used was the difference between II and I mm.,—i.e., IO mm. The object of using the smaller depth of the solution was to bring out more clearly, in the case of hydrated salts, the second water-band:

	1 4	ABLE	 v .
MaC1.			

	CaCl <sub>2</sub> 5 · 38 N		MgCl <sub>2</sub> 4.96 N		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> I . 02 N	
	1/I <sub>o</sub>	H <sub>2</sub> O	1/I <sub>0</sub>	$H_2O$	$I/I_{o}$	H <sub>2</sub> O
1085	84	84	82	84	79	82
1100	84	84	83	84	78	8r
1113	84	86	83	84	78	84
1138	86	85	82	83	77	83
1148	82	83	79	80	75	8o
1158	8o	79	77	77	73	77
1165	78	<b>7</b> 6	77	<i>75</i>	70	73
1172	76	72	74	70	66	69
1179	72	65	71	64	63	58
1186	63	55	62	52	55	48
1193	54	45	56	46	49	39
1200	45	40	48	42	43	34
1206	38	39	42	40	38	30
1213	35	39	39	38	36	29
1220	33	36	37	38	34	28
1227	32	36	36	38	32	28
1233	31	35	34	37	32	28
1241	32	35	34	34	31	28
1248	32	35	34	37	31	28
1250	33	35	34	38	31	28
1255	33	37	34	38	31	28
1268	35	38	33	38	30	29
1270	37	39	34	39	30	30
1285	38	40	35	40	30	31
1295	40	40	35	40	30	32
1300	42	41	36	41	30	32
1308	42	41	37	42	30	33
1316	45	41	39	42	30	33
1323	47	40	39	41	28	33
1330	46	39	40	40	27	32
1338	45	37	38	38	27	30
7701	CIVVVII	No 1016	.0			

Vol. CLXXVI, No. 1056-48

	CaCl <sub>2</sub> 5.38 N I/I <sub>o</sub>	$_{ m H_2O}$	MgCl <sub>2</sub> 4.96 N I/I <sub>0</sub>	$_{ m H_2O}$	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 1.02 N I/I <sub>0</sub>	H <sub>2</sub> O
1346	42	35	38	36	24	27
1352	40	32	34	33	22	24
1358	37	29	33	30	20	21
1365	33	25	29	26	18	19
1372	29	21	25	22	15	15
1387	19	13	18	15	IO	9
1404	12	10	12	ΙΙ	7	5
1418	7	6	7	9	4	3
1430	3	3	4	3	2	2
1445	2	I	I	I	I	I

When salts which are strongly hydrated in aqueous solution are not very concentrated, the difference between the transparency of the salt solution and that of water of the same depth of layer as the water in the solution is not so pronounced. This is what would be expected; since the total amount of water combined with the dissolved salt increases with the concentration of the solution. The data given in the following table bring out this fact:

			TABLE V.			
	CaCl <sub>2</sub> 2.69 N I/I <sub>0</sub>	$_{\mathrm{H_2O}}$	MgCl <sub>2</sub> 2.48 N I/I <sub>0</sub>	$_{ m H_2O}$	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 0.508 N I/I <sub>0</sub>	$_{ m H_2O}$
710	96	94	95	95	97	96
724	95	96	93	96	98	96
741	95	95	90	95	95	93
760	94	96	92	95	95	95
776	93	97	93	95	95	95
798	90	98	91	95	96	96
818	93	97	91	93	95	90
836	91	96	89	93	93	95
855	91	92	88	92	92	92
878	90	92	84	90	90	91
900	88	90	84	88	89	86
922	89	92	81	86	82	85
947	82	86	78	83	78	80
958	75	79	72	76	73	75
964	70	74	70	73	68	69
969	65	69	62	64	62	62
974	58	61	58	58	57	54
979	50	52	50	51	50	46
,982	44	47	46	46	46	42
985	40	43	42	43	43	40
991	39	41	40	41	41	39
1007	38	40	41	42	40	40

	CaCl <sub>2</sub> 2.69 N		MgCl <sub>2</sub> 2.48 N		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> 0.508 N	
	$I/I_{\circ}$	$H_2O$	III.	H <sub>2</sub> O	I I.	H <sub>2</sub> O
1013	39	42	40	44	40	40
1019	40	43	40	44	41	41
1025	43	45	44	41	43	43
1032	45	47	47	44	45	46
1037	48	50	50	• 46	47	48
1042	51	52	52	48	49	49
1046	56	56	56	54	53	54
1059	61	59	58	55	60	59
1065	65	64	64	62	59	62
1072	69	67	6 <del>7</del>	64	63	65
1078	70	69	69	67	65	69
1085	72	72	72	68	68	72
1100	73	73	73	71	69	73
1113	72	74	74	72	68	74
1138	72	74	74	70	67	72
1148	66	69	69	67	64	67
1158	67	62	62	60	58	62
1165	57	58	58	58	54	54
1172	52	51	53	52	47	46
1179	46	39	42	42	39	35
1186	30	27	31	27	28	25
1193	20	19	21	20	20	16
1200	13	14	15	15	14	12
1206	12	ΙI	12	13	12	10
1203	II	ΙΙ	12	12	II	10
1220	ΙΙ	10	ΙΙ	ΙΙ	II	10
1227	10	9	IO	10	IO	9

The depth of layer of the different solutions for which the results are recorded in the above table was the difference between 21 and 1 mm.,—i.e., 20 mm. The results are, therefore, comparable with those recorded in Table III, the difference being a difference in the concentrations of the solutions used. It will be seen by a glance at the table, that the difference between the transmission of the solution and that of water of the same depth as the water in the solution, is very much less for the more dilute than for the more concentrated solutions. As has already been pointed out, this is exactly what would be expected in terms of the solvate theory applied to the phenomenon in question.

Considerable work was done in *comparing directly* the transmission of a solution, and that of water having the same depth as the water in the solution in question. The deflection of the

radiomicrometer as given by the solution is in the column marked "I sol.," and the deflection as given by water having the same depth as water in the solution is given in the column marked " $I_0H_2O$ ."

The results obtained for aluminium sulphate having a concentration 1.02 N, and for 4 N potassium chloride are given in the following table. The depth of solution used was 20 mm., and the depth of water that of the water in the solutions in question.

TABLE VI.

		I ADEL VI.		
	I sol. Al <sub>2</sub> (So <sub>4</sub> ) <sub>3</sub>	I <sub>o</sub> H <sub>2</sub> O	I sol. KCl	I₀ H₂O
710	50	51	53	53
724	58	58	56	56
741	62	63	67	' 68
760	72	72	77	77
776	75	<b>7</b> 6	88	90
798	83	83	98	99
818	82	82	108	109
836	93	94	116	116
855	97	97	124	124
878	105	105	129	130
900	105	105	140	138
922	112	112	140	140
947	113	113	142	142
958	109	106	136	136
964	107	100	129	125
969	104	93	118	116
974	98	83	108	106
979	93	7.3	92	92
982	82	66	83	83
985	80	64	78	8o
991	78	62	78	8o
1007	78	65	78	81
1013	74	65	81	85
1019	77	68	84	88
1025	80	75	96	96
1032	84	77	100	101
1037	91	84	112	108
1042	92	92	119	116
1046	99	99	125	120
1059	105	105	141	136
1065	109	112	150	145
1072	114	119	159	153
1078	118	125	164	158
1085	122	132	168	164

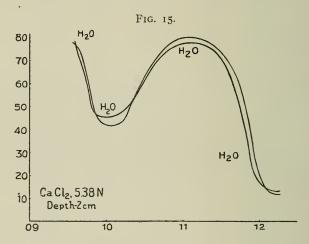
	$I \text{ sol.}$ $Al_2(So_4)_3$	I <sub>o</sub> H <sub>2</sub> O	I sol. KCl	<i>I</i> ₀ H₂O
1100	128	140	176	172
1113	129	142	178	175
1138	127	142	174	170
1148	123	131	164	162
1158	112	118	161	159
1165	108	III	157	154
1172	99	94	132	126
1179	87	74	107	100
1186	68	49	73	66
1193	54	35	50	48
1200	42	26	24	36
1206	35	23	39	32
1213	30	21	25	30
1220	28	20	24	29
1227	26	19	24	28
1241	24	19	23	26
1255	23	18	25	27

In this work duplicate measurements were made with the radiomicrometer for nearly every solution of all the substances worked with at the various wave-lengths studied. It was found that the readings for the different solutions of the same substance having the same concentration were, for a given wavelength, different from one another to the extent of somewhat less than 2 per cent. From this it seems fair to assume that the error in our work was not greater than 2 per cent.

An examination of the tables of data for potassium chloride, ammonium chloride, and ammonium nitrate,-that is, for those substances which, in aqueous solutions, combine with very little water, as was demonstrated by the freezing-point method, shows that for all wave-lengths studied the solution, and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent. When we began this work, we supposed that the water in the solution, whether it was combined with the dissolved substance or not, would have the same power to absorb light as so much pure solvent water. We shall now see that such is not the case.

The results for the above-named substances were not plotted in the form of curves, since the curve for water and for the solution would practically coincide with one another; the dissolved substance having very little absorption over the region of wavelengths studied in this investigation.

When we turn to the data in Tables III and IV, very different relations manifest themselves. These are the data for calcium chloride, magnesium chloride, and aluminium sulphate,—that is, for salts which, in aqueous solution, are strongly hydrated, as was shown by the earlier work in this laboratory.<sup>60</sup> The solution in these cases is often more transparent than the same amount of water that is contained in the solution.



That these relations may appear the more clearly, the results obtained for the above-named salts are plotted as curves in Figs. 15 to 20. Fig. 15 is the curve for calcium chloride having a depth of 20 mm. This was obtained by dividing the deflection produced by 21 mm. of the solution by that produced by 1 mm. of the solution. On the same sheet we have the curve for water having a depth equal to that of the water in the calcium chloride. This curve for water was also obtained by the "differential" method,—*i.e.*, by dividing the deflections produced by the deeper solution by those obtained with the more shallow solution; the difference in the depths of water in the two cases being just equal

<sup>60</sup> Carnegie Institution of Washington, Publication No. 60.

to the depth of water in 20 mm. of the solution in question. Fig. 16 is the curve for calcium chloride with a depth of layer of 10 mm. (11-1). The data from which the curve was plotted are contained in Table IV. The smaller depth of solution was used so that the water-band between  $1.2\mu$  and  $1.3\mu$  would come out more distinctly. The results for this solution, like those for all the others, are compared with the absorption of a depth of water equal to that of the water in the solution. The absorption of the water in this, as in all other cases, was obtained by the "differential" method.

Fig. 17 is the curve for magnesium chloride having a depth of 2I - I = 20 mm. and the corresponding water curve. The data from which these curves are plotted are given in Table III.

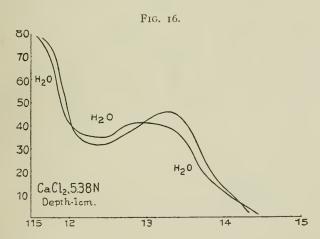


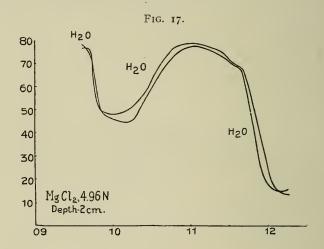
Fig. 18 is the curve for magnesium chloride having a depth of 1 cm., also obtained by the "differential" method. These data are taken from Table IV.

Fig. 19 is the curve for aluminium sulphate having a depth of 2I - I = 20 mm, and the corresponding absorption curve for water.

Fig. 20 is the curve for aluminium sulphate having a depth of II - I = I0 mm. and the corresponding water curve.

Fig. 15 shows the relative absorption of water and of the solution of calcium chloride having a concentration of 5.3 normal and a depth of 20 mm. The corresponding water curve is marked throughout by the symbol " $\rm H_2O$ ." The solution is the more

transparent from  $0.9\mu$  to nearly  $1\mu$ . The water then becomes the more transparent over a short region of wave-lengths. From  $1.05\mu$  to  $1.2\mu$  the solution is the more transparent. In this region the solution becomes as much as 25 per cent. more transparent than the pure water, as can be seen by comparing the points on the "water" curve with the corresponding points on the curve for the solutions which are vertically above the points on the water curve. The water becomes appreciably more transparent only at and near the bottom of the "water-band" having a wavelength of approximately  $1\mu$ . This is the effect that we would expect to get if the dissolved substance exerted a "damping" effect on the absorption of light by water.

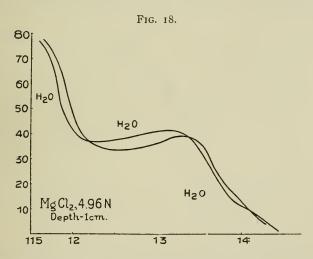


It will be recalled that the salts which do not form hydrates show, in aqueous solution, practically the same absorption as the corresponding amount of water. It would, therefore, seem reasonable to account for the differences in the case of non-hydrating and strongly hydrating salts, as due to the water of hydration, or the water that, in this case, is combined with the calcium chloride.

The curves in Fig. 16 are for a smaller depth of the same solution of calcium chloride. This figure brings out the same general relations as were shown in Fig. 15. The water curve in the region  $1.25\mu$  is above that of the solution, showing that water in this region for the more shallow depth of solution is

more transparent than the solution. The additional feature brought out by this figure is the water-band in the region  $1.4\mu$  to  $1.5\mu$ . After the first-named water-band is passed the solution becomes more transparent than the water, and remains so until the wave-length  $1.42\mu$  is reached. Here both the solution and the water are practically opaque, as is shown by both the curves approaching the abscissæ.

The curve for magnesium chloride having a depth of 20 mm. is almost exactly a duplicate of that for calcium chloride having the same depth. Practically the only difference worthy of mention is in the region from 1.0 $\mu$  to 1.1 $\mu$ . In the case of magnesium chloride the water remains the more transparent over this region

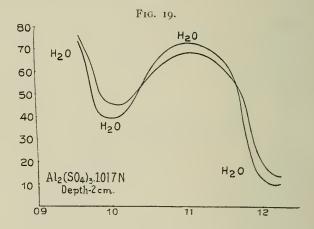


of wave-lengths. In the case of calcium chloride the solution is the more transparent over this region. The difference in the transparency of the water and the solution throughout the region is, however, not very great. From 1.1µ toward the longer wavelengths, as we come down the descending arm of the curve towards the second water-band, the water in the case of the magnesium chloride, as in the case of calcium chloride, becomes much more transparent than the solution; the differences here being of the same order of magnitude as those with calcium chloride.

Fig. 18 gives the results for magnesium chloride with a depth of layer of 1 cm. The same relations hold in Fig. 18 as in Fig. 17, for the relative transparency of the water and of the solution.

The water becomes the more transparent from  $1.22\mu$  to  $1.34\mu$ . For the longer wave-lengths the solution becomes more transparent until the region  $1.41\mu$  is passed. For wave-lengths longer than  $1.41\mu$ , the transmission of both solution and water is practically zero,—that is, they both become opaque to the longer wave-lengths.

The results in Fig. 19 bring out some new features of interest and importance. These are the results that were obtained with aluminium sulphate. The new feature shown by the curve for aluminium sulphate, as compared with those for calcium chloride and magnesium chloride, is that at the minimum of the curve corresponding to wave-length  $1\mu$ , the solution is more transparent

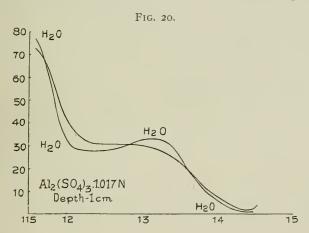


than the corresponding water. Beyond the wave-length 1.04 $\mu$ , the water becomes the more transparent with aluminium sulphate as with magnesium chloride. Beyond the wave-length 1.06 $\mu$ , the solution becomes more transparent in this case as with magnesium chloride and calcium chloride.

If we turn to Fig. 20 the relations are as follows: In the region of 1.2 $\mu$  the water is the more opaque. From 1.209 $\mu$  to 1.306 $\mu$  the water becomes the more transparent. From 1.306 $\mu$  to the longest wave-length studied, the solution again becomes more transparent than the corresponding layer of water.

An examination of all the results thus far obtained, bearing on this problem, leads us to conclude that the greater transparency of the solution as compared with the water in the solution, must be due to some action of the dissolved substance on the solvent water. The question remains, What is this action?

We have seen from our earlier work on the absorption spectra of solutions, which has been in progress in this laboratory continuously for the past eight years, that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first shown by Jones and Anderson. and a large number of examples of this effect have since been found by Jones and Strong. We interpreted the effect of the solvent on the power of the dissolved substance to absorb light, as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number



of facts that were brought to light for the first time by the investigations of the absorption spectra of solutions which have been carried on in this laboratory. Many of the phenomena which were thus explained, it seemed, could not be explained in terms of any other suggestion that has thus far been made. In a word, the solvate theory of solution, as proposed by Jones about fourteen years ago, 63 to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions that we use in the laboratory, and not simply a theory of ideal

<sup>61</sup> Carnegie Institution of Washington, Publication No. 110.

<sup>62</sup> Ibid., Nos. 130 and 160.

<sup>63</sup> Amer. Chem. Journ., 23, 103 (1900).

solutions as the theory of electrolytic dissociation alone must be regarded, has served good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions of dissolved substances.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution, and by a layer of water equal in depth to that of the water in the solution, is, to within almost the limit of experimental error, the same.

For those substances, however, which have been shown to form complex hydrates, the absorption of light by their solutions, and by a layer of water equal in depth to that of the water in the solution, is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, the solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to us to be, that the part of the water that is combined with the dissolved substance, has a smaller power to absorb light than pure, free, uncombined water. The fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favor of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

We have carried out similar investigations with aluminium nitrate, but the concentration of the strongest solution that could be obtained was not sufficiently great to show the phenomenon in question. We, therefore, do not incorporate the results obtained with this substance. That the solutions must be very concentrated to show clearly the phenomenon with which we are dealing, is shown by the results given in Table V. Here the solutions of the three salts in question that were used, are more dilute than those for which the results are tabulated in Tables III and IV. An examination of this table will show that the phenomenon in question does not manifest itself to anything like the same extent as with the more concentrated solutions. This is exactly

what we would expect in terms of the solvate theory of solutions. The more concentrated the solution, the larger the total amount of the water present combined with the dissolved substance. If combination between water and the dissolved substance explains the facts recorded in this paper, then the larger the amount of water present that is combined with the dissolved substance, the more pronounced the phenomenon in question.

The results obtained with aluminium sulphate bring out the same facts shown by calcium chloride and magnesium chloride. They, however, show in addition, that water is more transparent in the region of 1.1\mu and more opaque at 1\mu. That the sulphate should not agree throughout with the chlorides is really not surprising, since the sulphates show abnormal results in almost every particular. This is probably due, in part at least, to the large amount of polymerization which the sulphate molecules in general undergo in the presence of even water as a solvent. It should also be remembered in the present connection, that, while calcium chloride and magnesium chloride crystallize with only six molecules of water, and are, therefore, only largely hydrated, aluminium sulphate crystallizes with 18 molecules of water and is, therefore, very largely hydrated.

The results in Table VI are, as has already been stated, the radiomicrometer deflections for a solution of aluminium sulphate, and those for water having the same depth as the water in the solution in question, and the corresponding data for potassium chloride. A comparison of the two columns for potassium chloride and its corresponding water, shows that the two are almost equally transparent to all the wave-lengths studied.

A comparison of aluminium sulphate with its corresponding water, brings out the phenomenon that we are now discussing in a very pronounced manner. It is for this reason that the data in this paper are given.

One other relation of a general character should be pointed out. The curves upon all six of the figures show that the addition of salt to water shifts the absorption towards the longer wavelengths. This is analogous to what has already been found by Jones and Uhler,<sup>64</sup> Jones and Anderson,<sup>65</sup> Jones and Strong,<sup>66</sup>

<sup>64</sup> Carnegie Institution of Washington, Publication No. 60.

<sup>65</sup> Ibid., Publication No. 110.

<sup>66</sup> Ibid., Publications Nos. 130 and 160.

and Guy and Jones,<sup>67</sup> when the absorption of salts as affected by the water present was studied. It was found that rise in temperature and increase in the concentration of the solution both tended to shift the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and increase in the concentration of the solution tended to simplify the hydrates in combination with the particles of the salt. The resonator within this simplified system seems to vibrate so as to shift the absorption bands towards the red.

The effect of the salt on the absorption of the water, is the same as that of rise of temperature and increase of concentration on the absorption of the dissolved substance. We should naturally look for a similar explanation of the two sets of phenomena. It has been suggested by Dr. Guy that the effect of the salt on the absorption of light by water may be due to the breaking down of the associated molecules of water by the dissolved substance. This would be in keeping with the discovery made by Jones and Murray, 68 that one associated substance when dissolved in another associated substance diminishes its association.

In terms of this explanation, however, it is a little difficult to see why non-hydrated salts, such as were used in this work, do not also diminish the association of water and cause a shifting of its absorption bands towards the longer wave-lengths. It may be that the effect of the dissolved substance in breaking down the association of the water, is pronounced only in the case of water of hydration, or the water that is combined with the dissolved substance, and that the explanation offered above is fundamentally correct.

We wish to express our thanks to Prof. A. H. Pfund, who has made many valuable suggestions during the progress of this phase of the work. We would also express our thanks to Dr. E. P. Wightman, who has kindly drawn the curves for us, and to Dr. E. J. Shaeffer, who has assisted in preparing the solutions, and in making the readings.

### SUMMARY AND DISCUSSION.

The following twelve independent lines of evidence bearing upon the solvate theory of solution have, then, been established:

<sup>&</sup>lt;sup>67</sup> Carnegie Institution of Washington, Publication No. 190, Amer. Chem. Journ., 49, 1 (1913).

<sup>68</sup> Amer. Chem. Journ., 30, 193 (1903).

1. Relation between water of crystallization and lowering of the freezing-point of water.

2. Relation between water of crystallization and temperature of crystallization.

3. Minima in the boiling-point curves.

- 4. Hydrating power and temperature coefficients of conductivity.
- 5. Dissociation as measured by the freezing-point method, and by the conductivity method.

6. Hydrating power of the ions and their velocities.

- 7. Action of a salt with hydrating power on another salt in the same solution.
  - 8. Work in mixed solvents.
- 9. Evidence for solvation based upon the power of solutions to absorb light. Work of Jones and Uhler, on the effect of concentration, dehydrating agents, etc.
- 10. Work of Jones and Anderson on absorption spectra, in which the presence of "solvate" bands was first detected. This showed that the solvate had an effect on the absorption of light, and this could be explained only as due to a combination between the solvent and the resonator, or something containing the resonator.
- 11. The work of Jones and Strong on absorption spectra established the existence of a larger number of "solvent" bands. They showed that these were formed by many salts, and in many solvents. They could even distinguish between the bands of a salt in a given alcohol and in its isomer. This was regarded as very important. The temperature work of Jones and Strong was also in keeping with the solvate theory.
- 12. The work of Jones and Guy on the effect of high temperature on the absorption spectra of aqueous solutions, and also on the effect of dilution, led to results which were all in keeping with the solvate theory.

The most important spectroscopic work of Jones and Guy, as bearing on the solvate theory of solution, is that in which the radiomicrometer was used. It was here shown that solutions of certain strongly-hydrated non-absorbing salts, are *more transparent* than pure water having a depth equal to that of the water in the solution. In the case of non-hydrated salts the solution

was the more opaque. This shows that water in combination with the dissolved substance—water of hydration—has less absorption than pure, free water. This is regarded as striking evidence that some of the water in the presence of salts which are shown by other methods to hydrate, is different from pure, free, uncombined water; and the simplest explanation seems to be that this is the combined water, or the water of hydration.

The above twelve independent lines of evidence all point to the general correctness of the view that when a salt is dissolved in a solvent, there is more or less combination between the salt, or the ions resulting from it, and the solvent. The magnitude of this solvation depends upon the nature of the substance and of the solvent.

The question then arises, Of what significance or scientific value is the establishing of the fact that there is more or less combination between the dissolved substance and the solvent? This has already been discussed in various connections.<sup>69</sup>

### SIGNIFICANCE OF THE SOLVATE THEORY OF SOLUTION.

The evidence for the solvate theory of solution which has been furnished in this laboratory as the result of somewhat more than a dozen years of investigation, has recently been brought together and briefly discussed. The evidence is so unambiguous and convincing, that ions and some molecules combine with more or less of the solvent, that it seems that it can now be accepted as a fact of science.

This, however, raises a number of questions: What relation does the solvate theory of solution bear to the theory of electrolytic dissociation?

Does the solvate theory help us to explain any of the apparent discrepancies in the theory of electrolytic dissociation? Does the solvate theory help us to explain the facts of chemistry in general and of physical chemistry in particular? Why is the nature of solution so important, not only for chemistry but for science in general?

<sup>69</sup> See especially my little book "A New Era in Chemistry," just published by the D. Von Nostrand Co.

<sup>&</sup>lt;sup>70</sup> Z. physik. Chem., 74, 325 (1910).

The Solvate Theory and the Theory of Electrolytic Dissociation.

When Arrhenius proposed the theory of electrolytic dissociation, the question was not even raised as to the condition of the ions in the solution, except that they behave as if they existed independently of one another in solution. The theory simply said that molecules of acids, bases, and salts in the presence of a dissociating solvent like water, break down to a greater or less extent into charged parts called ions; the cations or positively charged parts being electrically equivalent to the anions or negatively charged parts. The cations are usually simple metallic atoms carrying one or more unit charges of positive electricity. The cation might, however, be more or less complex, as illustrated by ammonium and its substitution products. The anion is usually complex, consisting of a larger or smaller number of atoms. It may, however, be an atom carrying negative electricity, as in the case of the halogen acids and their salts.

The degree of dissociation is determined by the nature of the acid, base, or salt. Strong acids and bases are greatly dissociated. Indeed, the degree of dissociation determines their strength. Nearly all of the salts are strongly dissociated compounds; there being, however, some exceptions; as, notably, the halogen salts of mercury, cadmium, and zinc. There are, however, considerable differences in the amounts to which salts in general are dissociated at the same dilution.

The quantitative evidence furnished by Arrhenius and others for the theory of electrolytic dissociation, is so convincing that few chemists of any prominence, who have carefully examined the evidence, have ever doubted the general validity of the theory; and the theory has become substantiated by such an abundance of subsequently discovered facts, that it has now become a law of nature and a fundamental law of chemical science.

Arrhenius saw and pointed out clearly the importance of ions for chemistry; and Ostwald and his pupils have shown that chemistry is essentially a science of the *ion*; molecules for the most part being incapable of reacting chemically with molecules; and Nernst has shown that the ion is the active agent in all forms of primary cells.

The theory of electrolytic dissociation, as already stated, does not raise the question as to the relation between the ion and

Vol. CLXXVI, No. 1056-49

the solvent. At the time that the theory was proposed, chemists did not know, and probably had no means of finding out, whether the ion is or is not combined with the solvent in contact with it. The solution of this problem remained for subsequent work.

Some of the many lines of evidence that ions and certain molecules are combined with a larger or smaller number of molecules of the solvent, and in many cases with a very large number of molecules of the solvent, have been recently discussed briefly by Jones in an article in the Zeitschrift für physikalische Chemie.<sup>71</sup>

The amount of the solvent combined with an ion is primarily a function of the nature of the ion or ions in the solution. It is, however, conditioned very largely by the dilution of the solution,

and also by the temperature.

The evidence, some of which is given in the paper referred to above, and the remainder in other publications of the results of investigations carried out in this laboratory during the past fourteen years, shows that the power of the ions to combine with the solvent is by no means limited to water and aqueous solutions, but is a property of solutions in general. The alcohols, acetone, glycerol,<sup>72</sup> etc., combine with certain substances dissolved in them; and it seems more than probable that all solvents combine with the dissolved substances to a greater or less extent. In a word, we do not have simply a theory of hydration, but a theory of solvation in general; which is an essential part of any generalization that would take into account the facts presented by solution.

The solvate theory of solution has been regarded in some quarters as a rival of the electrolytic dissociation theory of solution; if not directly antagonistic to it. Such is not at all the case. The solvate theory begins where the theory of electrolytic dissociation ends. The latter gives us the ions from molecules, and the former tells us what is the condition of the ions in the presence of a solvent after they are formed.

The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution.

<sup>&</sup>quot; "Evidence Obtained in this Laboratory during the Past Twelve Years for the Solvate Theory of Solution." Z. physik. Chem., 74, 325 (1910).

<sup>&</sup>lt;sup>72</sup> "Conductivity and Viscosity in Mixed Solvents," by H. C. Jones and Coworkers, Carnegie Institution of Washington, Publication Nos. 80 and 180.

Does the Solvate Theory Help to Explain Any of the Apparent Exceptions to the Theory of Electrolytic Dissociation?

Given the theory of solvation in solution, together with that of electrolytic dissociation, the first question that arises is, Does the former really aid us in explaining the phenomena presented by solutions?

Shortly after the theory of electrolytic dissociation was proposed, it was recognized, and repeatedly pointed out, that after all it is only a theory of "ideal solutions,"—i.e., very dilute solutions. It was shown not to be able to explain many of the phenomena presented by even fairly concentrated solutions. Indeed, it frequently could not deal quantitatively with the very solutions with which we work in the laboratory.

The explanation of this shortcoming was not fully seen, and an analogy was resorted to. It was pointed out that the laws of Boyle and Gay-Lussac for gases hold only for "ideal gases,"—i.e., dilute gases,—but do not hold for gases of any considerable concentration.

It was stated that the gas laws when applied to solutions could not be expected to hold more generally than when applied to gases, and there the matter was allowed to rest.

In the early days of the theory of electrolytic dissociation, it was, however, pointed out, that we have a fairly satisfactory explanation of why the simple gas laws do not hold for concentrated gases; this being expressed in the equation of Van der Waals; while no analogous explanation was offered in the case of solutions.

That this point was well taken is obvious. A theory of solution to be of the greatest value must be applicable to all solutions; regardless of the nature of the substance; regardless of the nature of the solvent; and regardless of the concentration of the solution.

The explanation of these apparent exceptions to the theory of electrolytic dissociation presented by concentrated solutions has been furnished by the solvate theory. We now know that, for solutions in general, a part of the solvent is combined with the dissolved substance. While the amount of the solvent combined with any one ion is greater the more dilute the solution, at least up to a certain point, the total amount of the solvent in combina-

tion with the dissolved substance is greater the more concentrated the solution.

That the amount of combined solvent may become very great, even relative to the total amount of solvent present, can be seen from the following facts: In a normal solution of calcium chloride about two-fifths of the total water present is combined with the dissolved substance. In a three-normal solution of calcium chloride about five-sevenths of the total water is combined.

In the case of a normal solution of aluminium chloride in water, about five-eighths of the water present is combined with the dissolved substance, while in a two-normal solution about five-sixths of the water present is in a state of combination.<sup>73</sup>

What we suppose to be a normal solution of calcium chloride is, therefore, more than one and one-half times normal; while what we suppose to be a three-normal solution is in reality more than eight times normal. In the case of aluminium chloride, what we suppose to be a normal solution is more than twice normal, while what we prepare as a twice normal solution is about twelve times normal.

These few facts, taken from thousands of a similar character, show that even fairly concentrated solutions are much more concentrated than we would suppose from the method of their preparation; while very concentrated solutions are many times more concentrated than, without the facts of solvation, we should be led to think.

The general conclusion is that even fairly concentrated solutions are much stronger than if no solvation occurred; and are much more concentrated than we are accustomed to consider from the amount of substance added to a given volume of the solution—more or less of the water present being in combination and only the remainder playing the rôle of solvent. Without the theory of solvation, we have hitherto regarded all the water present as acting as solvent.

We should, therefore, not expect the laws of gases to apply to such solutions, when we had no idea what was their concentration. Now that we know their concentration, we find that the laws of gases are of as general applicability to solutions as to

<sup>&</sup>lt;sup>73</sup> "Hydrates in Aqueous Solution," by H. C. Jones and Coworkers, Carnegie Institution of Washington, Publication No. 60.

gases, holding not simply for dilute, but also for concentrated solutions.

The theory of electrolytic dissociation, supplemented by the theory of solvation, is, then, not simply a theory of dilute or "ideal" solutions, but a theory of solutions in general.

# Does the Solvate Theory Aid Us in Explaining the Facts of Chemistry in General and of Physical Chemistry in Particular?

To answer this question at all fully would lead us far beyond the scope of this paper. A few facts bearing upon this question can, however, be taken up. Take, for example, the action of the hydrogen ion both in the formation and the saponification of esters. In the presence of the alcohols the hydrogen accelerates greatly the velocity with which an ester is formed; while in the presence of water it causes the ester to break down into the corresponding acid and alcohol.

In terms of ordinary chemical conceptions it is difficult, not to say impossible, to interpret these reactions—the hydrogen ion under one set of conditions undoing what under other conditions it effected.

In terms of the solvation theory these reactions admit of a very simple interpretation. While the hydrogen ion is not strongly solvated, yet work in this laboratory has shown that all ions are more or less solvated. In the presence of alcohol the hydrogen ion therefore combines with a certain amount of this solvent. The hydrogen ion, plus the alcohol combined with it, unites with the organic acid, forming complex alcoholated ions, which then break down, forming the ester.

On the other hand, the hydrogen ion in the presence of water combines with a certain amount of this solvent. The hydrated hydrogen ion, together with the water united with it, combines with the ester, forming a complex hydrated ion, which then breaks down into the corresponding acid and alcohol, setting the hydrogen ion free again.

For a fuller discussion of this reaction see the paper by E. Emmet Reid.<sup>74</sup>

<sup>74</sup> Amer. Chem. Journ., 41, 504 (1909).

A reaction analogous to the above is that of hydrogen ions on amides in the presence of water, on the one hand, and of alcohol on the other. In the presence of water the hydrated hydrogen ion combines with the amide, forming a complex hydrated ion which then breaks down, yielding ammonia and acid, the ammonia, of course, combining with the acid.

In the presence of alcohol the alcoholated hydrogen ion combines with the amide, forming a complex alcoholated ion, which then breaks down into ammonia and the ester of the acid in

question.

Hydrogen ions in a mixture of water and alcohol, which would contain both hydrated and alcoholated hydrogen ions, give both reactions simultaneously; but, as Reid has pointed out, in the presence of an equal number of molecules of water and alcohol, the tendency of the hydrogen ion to hydrate is greater than the tendency to form alcoholates; and under these conditions the first reaction proceeds much more rapidly than the second.<sup>75</sup>

A very large number of types of reactions could be discussed illustrating this same point,—i.e., the value of the solvate theory

in interpreting chemical reactions.

When we turn to physical chemical processes, the solvation of the ions has to be taken into account at every turn. The velocities of the ions are, of course, a function of the degree of their solvation; and the behavior of the ions, both chemically and physically, is a function of their velocities. The effect of dilution, and especially of temperature on reaction velocities, is largely a question of the velocities of the ions present, which, in turn, are a function of the degree of their solvation.

In determining the actual concentration of a solution, the amount of the solvent combined with the ions must be taken into account, as has already been pointed out; and without knowing the actual concentrations of solutions quantitative chemistry

would be impossible.

The solvate theory has thrown a flood of light on the whole subject of the conductivity of solutions, or the power of the ions to carry the electric current. It has shown us why the conductivity of lithium salts is less than that of sodium and potassium; notwithstanding the fact that the lithium ion is much smaller

<sup>&</sup>lt;sup>15</sup> Amer. Chem. Journ., 41, 509 (1909).

and lighter than the atom of sodium and potassium. We now know that the lithium ion is much more hydrated than the ions of sodium and potassium, and the mass of the moving ion is

really much greater than that of sodium or potassium.

When we come to the temperature coefficients of conductivity, the solvate theory has enabled us to interpret results which, without its aid, would be meaningless. We now know why ions with the greater hydrating power have the larger temperature coefficients of conductivity. We know why ions with the same hydrating power have approximately the same temperature coefficients of conductivity; and why dilute solutions have larger temperature coefficients of conductivity than concentrated solutions; 76 and we could multiply examples almost without limit, did space permit, of the effect of the solvate theory on physical or general chemistry.

Why is the Nature of Solutions of such Vital Importance not only for Chemistry but for Science in General?

The fact is well recognized that modern physical or general chemistry has reached out into nearly every branch of science, and has had an important influence on many of them. The question arises: Why is this the case? The answer is that physical or general chemistry is primarily a science of solutions.

This answer may not at first sight appear to be self-evident, but a moment's thought will show its general correctness. The whole science of chemistry is primarily a science of solutions in the broad sense of that term. By solutions is meant not simply solutions in liquids as the solvent; but solutions in gases and in solids as well; and not simply solutions at ordinary temperatures, but also at elevated temperatures. If we think of chemical reactions in general, we will realize what a small percentage of them take place out of solution. Therefore, the nature of solution is absolutely fundamental for chemistry. This applies not simply to general chemistry, including the chemistry of carbon; but also to physiological chemistry, which deals almost entirely with solutions in one solvent or another.

When we turn to physics we find solutions not playing as prominent a rôle as in chemistry, but nevertheless coming in in

<sup>&</sup>lt;sup>76</sup> Jones, Amer. Chem. Journ., 35, 445 (1906).

many places. The primary cells, secondary cells, electrolysis, polarization, diffusion, viscosity, surface-tension, are all phenomena in which the physicist is interested, and all depend for their existence upon solution.

When we turn to the biological sciences we find that solution is almost as important as for chemistry. Take animal physiology; here we have to deal very largely with solution in the broad sense of that term. The same remark applies to physiological botany; and solutions are very important for both animal and vegetable morphology, especially in their experimental developments. Bacteriology is fundamentally connected with solutions, and pharmacology is based upon solutions either without or within the body of the animal.

Solution in the broad sense is as fundamental for geology as for chemistry. The igneous rocks were solutions of one molten mass in another, and sedimentary deposits came down for the most part from solutions in water. The minerals crystallized out from solutions, and solutions of various substances, such as carbon dioxide, are to-day weathering the rocks and continually changing the appearance of the face of the globe.

An examination of facts such as those referred to above, will show the truth of the statement that the relation of physical or general chemistry to solutions, is the prime reason why physical or general chemistry is so closely related to so many other branches of natural science.

This alone would show the importance of a true and comprehensive theory of solutions, not alone for physical or general chemistry, but for the natural sciences in general.

#### BIBLIOGRAPHY.

It has seemed desirable, at the close of this *résumé* of the more important lines of evidence bearing on the solvate theory, to give a bibliography of the papers and monographs which have been published from this laboratory dealing directly and indirectly with the subject.

#### PAPERS.

2. Chambers and Frazer: "On a Minimum in the Molecular Lowering

I. Jones and Chambers: "On Some Abnormal Freezing-point Lowerings Produced by Bromides and Chlorides of the Alkaline Earths." Amer. Chem. Journ., 23, 89 (1900).

of the Freezing-point of Water, Produced by Certain Acids and Salts." Amer. Chem. Journ., 23, 512 (1900).

3. Jones and Getman: "The Lowering of the Freezing-point of Water Produced by Concentrated Solutions of Certain Electrolytes, and the Conductivity of Such Solutions." *Amer. Chem. Journ.*, 27, 433 (1902).

4. Jones and Getman: "The Molecular Lowering of the Freezing-point of Water Produced by Concentrated Solutions of Certain Electrolytes." Zeit-

schr. f. physik. Chemie, 46, 244 (1903).

- 5. Jones and Getman: "A Study of the Molecular Lowering of the Freezing-point of Water Produced by Concentrated Solutions of Electrolytes." *Phys. Rev.*, 18,\*146 (1904).
- 6. Jones and Getman: "On the Nature of Concentrated Solutions of Electrolytes-Hydrates in Solution." Amer. Chem. Journ., 31, 303 (1904).
- 7. Jones and Getman: "Ueber das Vorhandensein von Hydraten in konzentrierten wässerigen Lösungen von Elektrolyten." Zeitschr. f. physik. Chemie, 49, 385 (1904).
- 8. Jones and Getman: "Ueber die Existenz von Hydraten in konzentrierten wässerigen Lösungen der Elektrolyte und einiger Nichtelektrolyte." Ber. d. chem. Ges., 37, 1511 (1904).
- 9. Jones and Getman: "The Existence of Alcoholates in Solutions of Certain Electrolytes in Alcohol." Amer. Chem. Journ., 32, 338 (1904).
- 10. Jones and Getman: "The Existence of Hydrates in Solutions of Certain Nonelectrolytes, and the Non-existence of Hydrates in Solutions of Organic Acids." Amer. Chem. Journ., 32, 308 (1904).
- II. Jones and Bassett: "The Approximate Composition of the Hydrates Formed by Certain Electrolytes in Aqueous Solutions at Different Concentrations." Amer. Chem. Journ., 33, 534 (1905).
- 12. Jones and Bassett: "Der Einfluss der Temperatur auf die Kristallwassermenge als Beweis für die Theorie von den Hydraten in Lösung." Zeitschr. f. physik. Chemie, 52, 231 (1905).
- 13. Jones and Bassett: "The Approximate Composition of the Hydrates Formed by a Number of Electrolytes in Aqueous Solutions; Together with a Brief General Discussion of the Results Thus Far Obtained." Amer. Chem. Journ., 34, 291 (1905).
- 14. Jones: "L'Existence d'Hydrates dans les Solutions Aqueuses d'Electrolytes." Journ. de Chimie Phys., 3, 455 (1905).
- 15. Jones and McMaster: "On the Formation of Alcoholates by Certain Salts in Solution in Methyl and Ethyl Alcohols." Amer. Chem. Journ., 35, 316 (1906).
- 16. Jones: "Die annähernde Zusammensetzung der Hydrate, welche von verschiedenen Elektrolyten in wässeriger Lösung gebildet werden." Zeitschr. f. physik. Chemie, 55, 385 (1906).
- 17. Jones and Uhler: "The Absorption Spectra of Certain Salts in Aqueous Solution as Affected by the Presence of Certain Other Salts with Large Hydrating Power." Amer. Chem. Journ., 37, 126 (1907).
- 18. Jones and Uhler: "The Absorption Spectra of Certain Salts in Nonaqueous Solvents, as Affected by the Addition of Water." Amer. Chem. Journ., 37, 244 (1907).

19. Jones and Pearce: "Dissociation as Measured by Freezing-point Lowering and by Conductivity—Bearing on the Hydrate Theory. The Approximate Composition of the Hydrates Formed by a Number of Electrolytes." Amer. Chem. Journ., 38, 683 (1907).

20. Jones and Stine: "The Effect of One Salt on the Hydrating Power of Another Salt Present in the Same Solution." Amer. Chem. Journ., 39, 313

(1908).

21. Jones and Anderson: "The Absorption Spectra of Neodymium Chloride and Praseodymium Chloride in Water, Methyl Alcohol, Ethyl Alcohol, and Mixtures of These Solvents." *Proceed. Amer. Philosoph. Soc.*, 47, 276 (1908).

22. Jones and Jacobson: "The Conductivity and Ionization of Electrolytes in Aqueous Solutions as Conditioned by Temperature, Dilution, and

Hydrolysis." Amer. Chem. Journ., 40, 355 (1908).

23. Jones: "The Present Status of the Solvate Theory." Amer. Chem.

Journ., 41, 19 (1909).

- 24. Jones and Anderson: "The Absorption Spectra of Solutions of a Number of Salts in Water, in Certain Non-aqueous Solvents, and in Mixtures of These Solvents with Water." Amer. Chem. Journ., 41, 163 (1909).
  - 25. Jones and Strong: "Die Absorptionsspektren gewisser Salzlösungen."

Physik. Zeitschr., 10, 499 (1909).

- 26. Jones and Strong: "The Absorption Spectra of Various Salts in Solution, and the Effect of Temperature on Such Spectra." Amer. Chem. Journ., 43, 37 (1910).
- 27. Jones and Strong: "The Absorption Spectra of Various Potassium, Uranyl, Uranous and Neodymium Salts in Solution; and the Effect of Temperature on the Absorption Spectra of Certain Colored Salts in Solution." *Proceed. Amer. Philos. Soc.*, 48, 194 (1909).
- 28. Jones and Strong: "The Absorption Spectra of Solutions—A Possible Method of Detecting the Presence of Intermediate Compounds in Chemi-
- cal Reactions." Amer. Chem. Journ., 43, 224 (1910).
  29. Jones and Strong: "The Absorption Spectra of Certain Uranyl and Uranous Compounds." Phil. Mag., April, 1910.
- 30. Jones and Strong: "Spectres d. Absorption des Solutions. Possibilité D. une Méthode pour Déterminer La Presence de composis intermédiares dans les Réactions Chimiques. *Journ. Chim. Phys.*, 8, 131 (1910).
- 31. Jones: "Im hiesigen Laboratorium während der vergangenen zwölf Jahre erhaltene auhastspunkte für die Existenz von Solvaten in Lösung." Zeit. phys. Chem., 74, 325 (1910).
- 32. Jones and Strong: "The Absorption Spectra of Certain Salts of Cobalt, Erbium, Neodymium, and Uranium, as Affected by Temperature and by Chemical Reagents." Amer. Chem. Journ., 45, 1 (1910).

33. Jones: "Sur la Position de la Theorie des Solvates." Journ. Chim.

Phys., 9, 217 (1911).

34. Jones and Strong: "The Absorption Spectra of Comparatively Rare Salts. The Spectrophotography of Certain Chemical Reactions, and the Effect of High Temperature on the Absorption Spectra of Non-aqueous Solutions." Amer. Chem. Journ., 47, 27 (1912).

- 35. Jones: "The Nature of Solution." JOURNAL OF THE FRANKLIN INSTITUTE, March, 1912, p. 217.
- 36. Jones: "Absorption Spectra and the Solvate Theory of Solution." Phil. Mag., May, 1912, p. 730.
- 37. Jones: "Die Absorptionsspektra von Lösungen." Zeit. phys. Chem., 80, 361 (1912).
- 38. Jones and Guy: "Die Absorptionsspektren wässeriger Lösungen von Neodym- und Praseodymsalzen, mit dem Radiomikrometer gemessen." *Phys. Zeit.*, 13, 649 (1912).
- 39. Jones and Guy: "The Absorption Spectra of Solutions as Affected by Temperature and by Dilution. A Quantitative Study of Absorption Spectra by Means of the Radiomicrometer." Amer. Chem. Journ., 49, 1 (1913).
- 40. Guy, Schaeffer, and Jones: "Die Anderung der Absorption des Lichtes durch Wasser infolge der Gegewart stark hydrierter Salze, nachgewiesen mit Hilfe des Radiomikrometers—ein neuer Beweis für die Solvattheorie des Lösungen." *Phys. Zeit.*, 14, 278 (1913). Also *Amer. Chem. Journ.*, 49, 265 (1913).

Guy and Jones: "The Absorption Spectra of a Number of Salts as Measured by Means of the Radiomicrometer." Amer. Chem. Journ., November, 1913.

# CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION IN AQUEOUS SOLUTIONS.

- 41. Jones and West: "A Study of the Temperature Coefficients of Conductivity in Aqueous Solutions, and on the Effect of Temperature on Dissociation." Amer. Chem. Journ., 34, 357 (1905).
  - 42. Jones and Jacobson: See above, No. 22.
- 43. Jones and White: "The Effect of Temperature and Dilution on the Conductivity of Organic Acids in Aqueous Solution." Amer. Chem. Journ., 42, 520 (1909).
- 44. Clover and Jones: "The Conductivities, Dissociations, and Temperature Coefficients of Conductivity between 35° and 80° of Solutions of a Number of Salts and Organic Acids." Amer. Chem. Journ., 43, 187 (1910).
- 45. White and Jones: "The Conductivity and Dissociation of Organic Acids in Aqueous Solution at Different Temperatures." Amer. Chem. Journ., 44, 159 (1010).
- 46. West and Jones: "The Conductivity, Dissociation, and Temperature Coefficients of Conductivity at 35°, 50°, and 65° of Aqueous Solutions of a Number of Salts." Amer. Chem. Journ., 44, 508 (1910).
- 47. Wightman and Jones: "A Study of the Conductivity and Dissociation of Organic Acids in Aqueous Solution between Zero and Thirty-five Degrees." Amer. Chem. Journ., 46, 56 (1911).
- 48. Harford and Jones: "The Conductivities, Temperature Coefficients of Conductivity, and Dissociation of Certain Electrolytes." Amer. Chem. Journ., 46, 240 (1911).
- 49. Winston and Jones: "The Conductivity, Temperature Coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution

from 0° to 35°. Probable Inductive Action in Solution, and Evidence for the Complexity of the Ion." Amer. Chem. Journ., 46, 368 (1911).

50. Wightman and Jones: "A Study of the Conductivity and Dissociation of Certain Organic Acids at 35°, 50°, and 65°." Amer. Chem. Journ., 48, 320 (1912).

51. Springer and Jones: "A Study of the Conductivity and Dissociation of Certain Organic Acids in Aqueous Solution at Different Temperatures."

Amer. Chem. Journ., 48, 411 (1912).

52. Howard and Jones: "The Conductivity, Temperature Coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution

at 35°, 50°, and 65°." Amer. Chem. Journ., 48, 500 (1912).

53. Shaeffer and Jones: "A Study of the Conductivity, Dissociation, and Temperature Coefficients of Conductivity of Certain Inorganic Salts in Aqueous Solution, as Conditioned by Temperature, Dilution, Hydration, and Hydrolysis." Amer. Chem. Journ., 49, 207 (1913).

54. Smith and Jones: "Conductivity, Temperature Coefficients of Conductivity, Dissociation, and Dissociation Constants of Certain Organic Acids

between o° and 65°." Amer. Chem. Journ., 50, 1 (1913).

55. Jones: "The Bearing of Hydrates on the Temperature Coefficients of Conductivity of Aqueous Solutions." Amer. Chem. Journ., 35, 445 (1906).

#### WORK IN MIXED SOLVENTS.

56. Jones and Lindsay: "A Study of the Conductivity of Certain Salts in Water, Methyl, Ethyl, and Propyl Alcohols, and in Mixtures of These Solvents." Amer. Chem. Journ., 28, 329 (1902).

57. Jones and Murray: "The Association of a Liquid Diminished by the Presence of Another Associated Liquid." Amer. Chem. Journ., 30, 193 (1903).

58. Jones and Bassett: "Determination of the Relative Velocities of the Ions of Silver Nitrate in Mixtures of the Alcohols and Water, and on the Conductivity of Such Mixtures." Amer. Chem. Journ., 32, 409 (1904).

59. Jones and Carroll: "A Study of the Conductivities of Certain Electrolytes in Water, Methyl and Ethyl Alcohols, and Mixtures of These Solvents. Relation between Conductivity and Viscosity." Amer. Chem. Journ., 32, 521 (1904).

60. Jones and Bingham: "The Conductivity and Viscosity of Solutions of Certain Salts in Mixtures of Acetone with Methyl Alcohol, with Ethyl

Alcohol and Water." Amer. Chem. Journ., 34, 481 (1905).

61. Jones, Lindsay and Carroll: "Ueber die Leitfähigkeit gewisser Salze in gemischten Lösungsmitteln: Wasser, Methyl, Athyl und Prophylalkohol." Zeit. phys. Chem., 56, 129 (1906).

62. Jones and McMaster: "The Conductivity and Viscosity of Solutions of Certain Salts in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Binary Mixtures of These Solvents." Amer. Chem. Journ., 36, 326 (1906).

63. Jones and Roniller: "The Relative Migration Velocities of the Ions of Silver Nitrate in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone, and in Binary Mixtures of These Solvents, Together with the Conductivity of Such Solutions." *Amer. Chem. Journ.*, 36, 443 (1906).

64. Jones, Bingham and McMaster: "Ueber Leitfähigkeit und innere Reibung von Lösungen gewisser Salze in den Lösungsmittelgemischen, Wasser, Methylalkohol, Athylalkohol, und Aceton." Zeit. phys. Chem., 57, 193, 257 (1907).

65. Jones and Veazey: "A Possible Explanation of the Increase in Viscosity which Results When the Alcohols are Mixed with Water; and of the Negative Viscosity Coefficient of Certain Salts When Dissolved in Water."

Amer. Chem. Journ., 37, 405 (1907).

66. Jones and Veazey: "Die Leitfähigkeit und innere Reibung von Lösungen gewisser Salze in Wasser, Methylalkohol, Athylalkohol, Aceton, und binären gemischen dieser Lösungsmittel." Zeit. phys. Chem., 61, 641 (1908).

- 67. Jones and Veazey: "Die Leitfähigkeit und innere Reibung von Tetraäthylammoniumjodid in Wasser, Methylalkohol, Athylalkohol, Nitrobenzol und binären gemischen dieser Lösungsmittel." Zeit. phys. Chem., 62, 44 (1908).
- 68. Kreider and Jones: "The Dissociation of Electrolysis in Non-aqueous Solvents as Determined by the Conductivity and Boiling-point Methods." Amer. Chem. Journ., 45, 282 (1911).
- 69. Jones and Mahin: "The Conductivity of Solutions of Lithium Nitrate in Ternary Mixtures of Acetone, Methyl Alcohol, Ethyl Alcohol, and Water; Together with the Viscosity and Fluidity of These Mixtures." Amer. Chem. Journ., 41, 433 (1909).
- 70. Jones and Mahin: "Conductivity and Viscosity of Dilute Solutions of Lithium Nitrate, and Cadmium Iodide in Binary and Ternary Mixtures of Acetone with Methyl Alcohol, Ethyl Alcohol, and Water." Zeit. phys. Chem., 69, 389 (1909).
- 71. Schmidt and Jones: "Conductivity and Viscosity in Mixed Solvents Containing Glycerol." Amer. Chem. Journ., 42, 37 (1909).
- 72. Guy and Jones: "Conductivity and Viscosity in Mixed Solvents Containing Glycerol." Amer. Chem. Journ., 46, 131 (1911).
- 73. Kreider and Jones: "The Conductivity of Certain Salts in Methyl and Ethyl Alcohols at High Dilutions." Amer. Chem. Journ., 46, 574 (1911).
- 74. Davis and Jones: "Leitfähigkeits- und negative Viskozitätskoeffizienten gewisser Rubidium und Ammoniumsalze in Glycerin und in gemischen von Glycerin mit Wasser von 25° to 75°." Zeit. phys. Chem., 81, 68 (1912).
- 75. Wightman, Davis, Holmes and Jones: "The Conductivity and Viscosity of Solutions of Potassium Iodide and Sodium Iodide in Mixtures of Ethyl Alcohol and Water." *Journ. Chim. Phys.*, November or December, 1913.
- 76. Davis, Hughes and Jones: "Conductivity and Viscosity of Solutions of Rubidium Salts in Mixtures of Acetone and Water." Zeit. phys. Chem., 1913.

#### MONOGRAPHS

on researches dealing directly or indirectly with the subject in hand, published by the Carnegie Institution of Washington:

1. HYDRATES IN AQUEOUS SOLUTION. Evidence for the Existence of Hydrates in Solution, Their Approximate Composition, and Certain

Spectroscopic Investigations Bearing Upon the Hydrate Problem. By Harry C. Jones, with the assistance of F. H. Getman, H. P. Bassett, L. McMaster, and H. S. Uhler. Carnegie Institution of Washington, Publication No. 60 (1907).

2. CONDUCTIVITY AND VISCOSITY IN MIXED SOLVENTS. A Study of the Conductivity and Viscosity of Certain Electrolytes in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone; and in Binary Mixtures of These Solvents. By Harry C. Jones and C. F. Lindsay, C. G. Carroll, H. P. Bassett, E. C. Bingham, C. A. Rouiller, L. McMaster, and W. R. Veazey. Carnegie Institution of Washington, Publication No. 80 (1907).

3. THE ABSORPTION SPECTRA OF SOLUTIONS of Certain Salts of Cobalt, Nickel, Copper, Iron, Chromium, Neodymium, Praseodymium, and Erbium in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone, and in Mixtures of Water with the Other Solvents. By Harry C. Jones and John A. Anderson. Carnegie Institution of Washington, Publication No. 110 (1909).

4. A STUDY OF THE ABSORPTION SPECTRA of Solutions of Certain Salts of Potassium, Cobalt, Nickel, Copper, Chromium, Erbium, Praseodymium, Neodymium, and Uranium, as Affected by Chemical Agents and by Temperature. By Harry C. Jones and W. W. Strong. Carnegie In-

stitution of Washington, Publication No. 130 (1910).

5. THE ABSORPTION SPECTRA OF SOLUTIONS OF COMPARA-TIVELY RARE SALTS, Including Those of Gadolinium, Dysprosium, and Samarium. The Spectrophotography of Certain Chemical Reactions, and the Effect of High Temperature on the Absorption Spectra of Non-aqueous Solutions. By Harry C. Jones and W. W. Strong. Carnegie Institution of

Washington, Publication No. 160 (1911).

6. THE ELECTRICAL CONDUCTIVITY, DISSOCIATION AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY FROM ZERO TO SIXTY-FIVE DEGREES OF AQUEOUS SOLUTIONS OF A NUM-BER OF SALTS AND ORGANIC ACIDS. By Harry C. Jones. The experimental work by A. M. Clover, H. H. Hosford, S. F. Howard, C. A. Jacobson, H. R. Kreider, E. J. Shaeffer, L. D. Smith, A. Springer, Jr., A. P. West, G. F. White, E. P. Wightman, and L. G. Winston. Carnegie Institution of Washington, Publication No. 170 (1912).

7. THE FREEZING-POINT, CONDUCTIVITY, AND VISCOSITY OF SOLUTIONS OF CERTAIN ELECTROLYTES IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL, ACETONE, AND GLYC-EROL, AND IN MIXTURES OF THESE SOLVENTS WITH ONE ANOTHER. By Harry C. Jones and Collaborators. (The seven collaborators in this monograph are Drs. C. M. Stine, J. N. Pearce, H. R. Kreider, E. G. Mahin, M. R. Schmidt, J. Sam Guy, and P. B. Davis.) Publication of the Carnegie Institution of Washington, No. 180 (1913).

8. THE ABSORPTION SPECTRA OF SOLUTIONS AS AFFECTED BY TEMPERATURE AND BY DILUTION. A QUANTITATIVE STUDY OF ABSORPTION SPECTRA BY MEANS OF THE RADIOMICROM-ETER. By Harry C. Jones and J. Sam Guy. Publication of the Carnegie Institution of Washington, No. 190 (1913).

Johns Hopkins University, Baltimore, September, 1913.

# NOTES FROM THE U.S. BUREAU OF STANDARDS.\*

The Bureau is issuing a supplement to Circular No. 38, on the testing of rubber. At a conference of manufacturers and users of rubber insulation, held in New York, December 7, 1911, it was decided to take steps to improve and standardize methods for analyzing rubber compounds. In pursuance of the decision reached, a committee, now known as the Joint Rubber Insulation Committee, was appointed to devise specifications and an analytical procedure for rubber insulating compounds.

After the first report of this committee had been adopted unanimously by the conference, it was submitted to the Bureau of Standards, at the request of the committee, for tentative approval and possible publication. Because of actual participation by the Bureau in the work of the committee, and because of the importance of the report it is now published as a supplement to Circular No. 38, "The Testing of Mechanical Rubber Goods." It is believed that the report is a long step in the direction of standard specifications and suitable methods of analysis, the preparation of which is peculiarly germane to the work of the Bureau of Standards, and that it should prove of great value to consumer and manufacturer alike.

The Bureau of Standards is issuing a preliminary circular on "The Testing of Barometers." It is issued in advance of the final results of the Bureau's investigations only in response to repeated requests for information. It will serve to describe in a general way the testing of mercurial and aneroid barometers at the Bureau of Standards, and to announce the fees which are charged for the various tests.

# CIRCULAR NO. 45, ON THE TESTING OF MATERIALS.

ANNOUNCEMENT was previously made of the issue of a circular on the testing of materials. The circular has now appeared and may be obtained upon application to the Bureau of Standards. The general importance in this subject makes it of interest to give a summary of the topics treated in this circular:

<sup>\*</sup> Communicated by the Bureau.

- I. Introduction.
  - 1. Purpose.
  - 2. Testing of Materials.
  - 3. Classes of Materials.
  - 4. Properties of Materials.
  - 5. Determination of Properties of Materials.
  - 6. The Measure of Quality.
  - 7. Specifications or Standards of Quality.
  - 8. Improvement of Specifications.
- II. General Information Concerning the Testing of Materials.
  - I. Choice of Tests.
  - 2. Sampling and Selection of Test Pieces.
  - 3. Application for Testing.
  - 4. Shipping Directions.
  - 5. Identification Marks.
  - 6. Time Required for Testing.
  - 7. Results of Tests and their Interpretation.
  - 8. Fees for Testing.
  - 9. For Whom Tests are Made.
- III. Special Information Concerning the Classes of Materials Tested.
  - I. Metals.
    - A. Metals and metal products: Definition, sources and uses, purposes of tests. Nature of tests: Chemical analysis, metallographic examination and heat treatment. Mechanical tests: Tension, compression, flexure, torsion, hardness, strain measurements. Miscellaneous physical tests: Sampling and testing under specifications.
    - B. Composite metal products: Plated and coated metals, enamels for cast iron and steel.
  - 2. Cements (hydraulic) and concrete.
    - A. Portland cement: Definition, sources, uses. Properties of cement: Chemical tests. Physical tests: soundness, time of setting, tensile strength, fineness, specific gravity, and sampling.
    - B. White cement.
    - C. Natural cement.
    - D. Raw cement materials.
    - E. Sand and stone screenings.
  - 3. Ceramics.
    - A. Clays and shales.
    - B. Clay products: clay building brick, architectural terra cotta, roofing tiles, floor tiles, glazed wall tiles, paving blocks and bricks, sewer pipe, drain tiles, porcelain and white ware, fire clays, fire-proofing for steel protection, refractories.
  - 4. Lime.
    - A. Burnt lime.
    - B. Hydrated lime.

- C. Raw materials for lime.
- D. Sand lime brick.
- 5. Stone.

Description and properties, tests: Compression tests, freezing tests, absorption tests, transverse tests, sampling.

- 6. Paint materials.
  - A. Colorants: Oil colors, water colors, tinting colors, enamel paints, stains.
  - B. Oils: Linseed oil, driers, volatile thinners.
  - C. Varnishes: Spirit varnishes, oil varnishes.
  - D. Tests.
  - E. Sampling.
- 7. Bituminous materials.

Definition and classification, use and general requirements, tests and interpretation of results, general statement, sampling.

- 8. Inks.
  - A. Writing inks: Description, tests, sampling.
  - B. Printing inks.
  - C. Stamp pad inks: Drying power, fastness of color, sampling.
- 9. Paper.

Definition and sources, uses, quality, and sampling.

- 10. Textiles.
  - A. Fibres, yarns, and fabrics.
  - B. Manila rope.
- 11. Rubber.

Tests: (a) Physical tests, (b) Chemical tests, sampling:
(a) Other conditions governing tests.

- 12. Leather.
- 13. Lubricating oils and greases.
  - A. Oils: Mechanical testing: (a) viscosity, (b) cold test, (c) flash and fire points. Chemical testing:
    - (a) Mineral acid, (b) Soap, (c) Ash, (d) Asphalt
    - test, (e) Organic acid, (f) Fat, (g) Carbonization.
    - (h) Evaporation and gumming, (i) Specific gravity.
  - B. Greases.
- 14. Chemicals.
- 15. Miscellaneous technical materials.
  - A. Electrical and magnetic materials.
  - B. Optical materials.
  - C. Thermal materials.
  - D. Water for boiler and technical use.
  - E. Miscellaneous materials.
  - F. Standard analyzed samples.
- 16. Testing of instruments used for testing materials.
- IV. Schedules of Fees.
- V. Publications.

Vol. CLXXVI, No. 1056-50

Aluminum as Flux. ROBERT GRIMSHAW. (Metal Industry, 11, 10, 425.)—Iron founders have long known that aluminum is an excellent flux. It oxidizes very easily and removes oxygen from the cast iron and steel, according to the formula  $Al_2 + O_3 = Al_2O_3$ evolving 391,000 calories, an amount of heat sufficient to raise the temperature of one kilogramme of iron 1400° C., or one pound 5544° F. This heat causes the sudden foaming of the mass. The energetic movement noticed in the pouring ladle brings the molecules in contact with air, which produces iron oxide; but this oxidation can be avoided by covering the melted iron or steel mass with sand or charcoal. If the melted metal does not attain a high temperature the effect of the addition of aluminum is almost nil. The amount of fluxing metal necessary depends on the quality of steel and the purpose of the casting. For steel with 0.5 per cent. carbon there should be added from 160 to 320 grains of aluminum per ton, while for a higher carbon steel only 150 to 250 grains are necessary.

Granacite. H. FISHER. (Zeit. Angew. Chem., xxv, 1327.)—Granacite, a form of granite found in Saxony, is especially suitable for towers, vessels, containers, etc., in the industrial manufacture of acetic acid and white lead, phosphoric acid, bromine, and alkali manufacture, and in the paper industry for sulphite liquors.

Action of Light on Coloring Matters. W. HARRISON. (J. Soc. Dyers and Col., xxviii, 225.)—Experiments are quoted to show that: (1) Light from the mercury arc lamp does not act relatively the same as sunlight on all colors. (2) A mercury light of high intensity does not act relatively the same as one of low intensity. (3) Cellulose is decomposed by the action of light and air, with formation of reducing substances. (4) In a vacuum under the influence of light from a mercury lamp, cellulose acts as a reducing agent, but in a vacuum under the influence of sunlight, cellulose has little reducing power. This explains why direct dyestuffs do not fade in a vacuum under the influence of sunlight. (5) Most dyestuffs do not fade in the absence of fibre and air; direct dyestuffs do not fade in the absence of fibre; basic dyestuffs do not fade in absence of air. (6) Basic dyestuffs usually fade owing to oxidation. (7) Under the influence of mercury light, wool is not so powerful a reducing agent as cellulose. (8) Radium emanation has a powerful destroying action on cellulose, and on many direct and basic dyestuffs and on indigo; indanthrene and Para red, on the contrary, are only slightly affected. (9) Light from a mercury lamp browns and tenders both wool and silk. (10) Many substances affect the rate of fading of dyestuffs; oils, for example, assist the fading of vat dyestuffs through oxidation, whilst dextrin appears to protect all colors. To explain these observations the author advances a theory based on Drude's explanation of color absorption.

# NOTES FROM THE CARNEGIE INSTITUTION OF WASHINGTON.

THE following publications have recently been issued:

No. 168. S. W. Burnham, "Measures of Proper-Motion Stars." Quarto, iv + 311 pages.

Micrometer measures made with the large telescope of the Yerkes Observatory from 1907 to 1912 of various stars having large, small, or uncertain proper-motions. These selected stars are of all magnitudes, from the faintest in Argelander to prominent naked-eye stars, and include, so far as possible, all those which have been heretofore compared by direct measures with other and fainter stars in the field. Independent differential values of the proper-motions are thus obtained for comparison with the results found from meridian observations. The latter values are frequently discordant and contradictory, and particularly so when the motions are small. The several values from the leading authorities on meridian-circle observations, Auwers, Newcomb, Porter, Boss, etc., and from the various standard star catalogues, are collected and compared. The greater number of proper-motion stars observed here are taken from the "General Catalogue of Double Stars." The others are selected from various sources and include stars of special interest, among others the Boss group of Taurus stars with a common movement in space, and small stars with supposed proper-motions taken from the Oxford and other astrographic catalogues. As a rule, each star is measured on three or more nights, and very faint comparison-stars selected which, it is safe to say, have no sensible motion which could affect the result obtained. No really faint star, not attached to and moving with a brighter star, has ever been shown to have any propermotion which could be detected by any method of observation to this time. Of course, it is to be presumed that the faintest and most distant stars have both proper-motion and parallax, and it is equally obvious that the one is as negligible as the other in all differential comparisons. A careful remeasurement of these

small stars after a suitable interval of time will give the movement of the principal stars with a degree of accuracy not yet attained by other methods.

No. 180.—Harry C. Jones and Collaborators, "The Freezing-point Lowering, Conductivity, and Viscosity of Solutions of Certain Electrolytes in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Glycerol, and in Mixtures of these Solvents with one Another." Octavo, vii + 214 pages, 85 text figures.

The seven pieces of work incorporated in this monograph are a continuation of the investigations recorded in monograph No. 80, published in 1907. The effect of one hydrated salt on the hydration of another hydrated salt was worked out with a number of pairs of salts. The dissociation of a number of salts was determined by the freezing-point and conductivity methods. It was shown that the atoms or ions with the smallest volumes have the greatest hydrating power. The relation between hydrating power and electrical density is discussed. The dissociation in the alcohols was determined by the improved conductivity method.

Three investigations had to do with the physical chemistry of glycerol as a solvent. The conductivity and viscosity of solutions in glycerol as a solvent were studied at different temperatures, glycerol being a liquid solvent with enormous viscosity. The temperature coefficients of both conductivity and viscosity in glycerol were very great. The salts of ammonium and rubidium were found to lower the viscosity of glycerol. The explanation of this phenomenon, offered by Jones and Veazey in monograph No. 80, for aqueous solutions, was found to apply equally well for solutions in glycerol as the solvent.

No. 186.—Carl Barus, "The Diffusion of Gases through Liquids, and Allied Experiments." Octavo, x + 88 pages, 38 text figures.

In 1900 the author began a series of experiments to determine the rate at which gases diffuse out of a submerged Cartesian diver through water. The method proved to be remarkably sensitive and the results striking. In the present volume the method is perfected, with a view to completing the measurements within a reasonably short interval of time. Diffusions of air, hydrogen, and oxygen into each other, through water and a variety of solutions, are investigated in detail and the diffusion constants determined. It is shown that a method of exploring the internal channels or physical pores of liquids is probably in question. In the course of the work a number of other applications are included; for instance, the disk of an absolute electrometer is floated on a Cartesian diver submerged in hydrocarbon oil, and the potential is measured absolutely by the pressure needed to just suspend the diver in the liquid. All these results are given in full and in most cases charted, the curves being often of singular complication. It is shown why diffusion frequently occurs against the apparent pressure gradient.

No. 190.—Harry C. Jones and J. S. Guy, "The Absorption Spectra of Solutions as Affected by Temperature and by Dilution: A Quantitative Study of Absorption Spectra by Means of the Radiomicrometer." Octavo, vii + 93 pages, 22 plates, 44 text figures.

A form of closed apparatus was devised and used for studying the absorption spectra of aqueous solutions up to 200°. It was found that the absorption bands widen with rise in temperature. The effect of dilution on the absorption spectra of solutions was also investigated over a range of dilution varying from I to 500. The absorption increased with the concentration, especially towards the red end of the spectrum. A radiomicrometer was built and used for study absorption spectra quantitatively. This permitted work at much greater wave-lengths than was possible by means of the grating spectroscope and photographic plate. The former was limited to \$2,600, while the latter can be used as far as λ30,000, and even farther. The effect of dilution was also studied quantitatively by means of the radiomicrometer, and interesting and important results were obtained in reference to the effect of dilution on the nature and position of the transmission bands. It was found that "free" water had a different absorption from "combined," and this was regarded as further evidence for the solvate theory of solution. The absorption spectra of a fairly large number of salts were mapped by means of the radiomicrometer.

The following works are in the course of preparation and will appear shortly:

No. 88.—V. BJERKNES and Collaborators, "Dynamic Meteorology and Hydrography."

This work constitutes an advanced mathematico-physical treatise on the dynamics and thermodynamics of the atmosphere and the ocean, the main aim being to develop rational methods, based on the principles of dynamics and thermodynamics, for the investigations in meteorology and oceanography.

PART III, DYNAMICS.

No. 161.—F. R. Moulton, in collaboration with Daniel Buchanan, Thomas Buck, Frank L. Griffin, William R. Longley, and William D. MacMillan, "Periodic Orbits."

A large part, though not all, of the periodic orbits treated in this book belong to the problem of three bodies. The first chapter contains certain theorems on implicit functions, the solutions of analytic differential equations, and a new treatment of linear homogeneous and non-homogeneous differential equations having periodic coefficients. The second contains a treatment of elliptic motion by the methods which have more general application. This is the simplest astronomical problem in periodic orbits. Certain additional methods are illustrated in the third chapter on the spherical pendulum, with new developments of certain elliptic functions. The fourth chapter treats of periodic motion about an oblate spheroid with applications to the motion of Jupiter's fifth satellite. The fifth chapter is devoted to a complete discussion of oscillating satellites in both two and three dimensions, in the case in which two of the bodies are finite and moving in circles, while the third is infinitesimal, and in which the centres of libration are collinear with the finite masses. Chapter VI is a treatment of the same problem by another method having important advantages in certain cases. Chapter VII is a discussion of the problem when the finite bodies move in elliptical orbits. Chapter VIII is a generalization of Lagrange's collinear solutions of the problem of three bodies to the general case of n bodies. Chapter IX is that of Chapter V for the equilateral triangular points of libration. Chapter X treats of the motion in the case

in which two masses are equal, the third infinitesimal or finite, and the three always occupying the vertices of an equilateral triangle. Chapter XI treats of satellites and inferior planets with application to the lunar theory. Chapter XII treats of superior planets. The problem of Chapter XIII is similar to that of Chapter XI, except that there are four or more bodies. Chapter XIV treats of the orbits of many small masses revolving around one large one. In all cases the existence of the periodic solutions is proved, methods of practically constructing them are given, and numerical illustrations are often added.

No. 165.—Derrick N. Lehmer, "Tables Giving a Complete List of Prime Numbers Between the Limits 1 and 10006721."

Until the completion of the author's Factor Table for the first ten million numbers the construction of a reliable list of primes was impossible, owing to the numerous errors still undetected in the old tables of factors. The list of primes herewith published is taken from the corrected tables of factors and has been checked by comparison with the results of the count of primes made independently of factor tables by Meissel and Bertelsen. The number of primes in each successive thousand as counted by Glaisher has also been compared with the number obtained from the list. The results indicate a very high degree of accuracy for the list.

The successive primes are arranged in columns of one hundred, there being fifty columns to the page. Each page thus serves to list 5000 primes. The total number of pages is 133, and therefore the total number of primes listed is 665,000. The page is identical in size with the page of the Factor Table. The arrangement enables one to tell at a glance the rank of any particular prime and the number of primes between any two given limits.

No. 192.—Ellsworth Huntington, with contributions by Charles Schuchert, A. E. Douglass, and Charles J. Kullmer, "The Climatic Factor, as Illustrated in Arid America."

This study of changes of climate is a continuation of the work described in the author's papers in Nos. 26, published 1905, and 73, issued in 1908. It deals mainly with the relation of

climate to geological, botanical, and archæological phenomena, but contains also a considerable amount of geographical description. The book begins with a discussion of the present climate of Arizona and New Mexico, and its effect upon the earth's surface and upon vegetation. Because of the aridity and scanty vegetation, deposits of alluvium are abundant and many are terraced. A consideration of whether these terraces are of climatic or tectonic origin leads to the conclusion that they are climatic, and that they indicate climatic pulsations during the period of human occupation. Numerous ruins, here and in Mexico, Yucatan, and Guatemala, point to the same conclusion and suggest the existence of at least three moist periods separated by times of aridity.

An independent investigation of the same problem, based on the method of Prof. A. E. Douglass, shows that the amount of rainfall may be determined from the thickness of rings of growth in trees. From measurements of 450 Sequoias in California a curve has been plotted showing the approximate pulsations of rainfall in California for 3000 years. Comparison with meteorological records suggests that the pulsations consist of an alternate weakening and strengthening of atmospheric circulation, whereby climatic zones are moved first poleward, then equatorward.

This conclusion leads to an attempt to determine the cause of changes of climate, including not only recent changes, but those of geological times, which are discussed by Professor Schuchert, who lays special emphasis upon the importance of broad crustal deformation. Such deformation, however, can scarcely account for glacial and interglacial epochs, and much less for the pulsations indicated by the California trees. Only the solar hypothesis seems adequate. This conclusion is tested by investigating the possibility of a connection between variations in sun spots and changes in the growth of trees. Such a connection seems to exist, and various phenomena suggest that apparent discrepancies are in reality results that would naturally be expected.

Chapters 2, 4, 5, 6, and 10 deal with the geological problem of the effect of aridity upon surface forms and upon subaërial deposits. The problem of the tectonic *versus* climatic origin of alluvial terraces in dry mountain regions is treated at length. Chapters 19, 20, and 21 discuss theories of climatic changes, special emphasis being given to the solar hypothesis as the cause

of changes of the magnitude of glacial epochs or less, and to crustal deformation as the cause of greater changes, such as glacial periods.

Inasmuch as botanical evidence is largely used in elucidating the climate of the past, Chapter 2 describes the arboreal desert of the southwestern United States. Chapters 11 and 14 discuss the relation of the thickness of rings of growth to climatic conditions, not merely in the case of the Sequoia of California, but among trees from all parts of the country. The evidence presented in Chapters 15, 16, and 17 suggests that in equatorial regions plant formations may be displaced by climatic changes with a degree of rapidity which must cause the process of natural selection to act with greater speed than is commonly supposed.

The climate of the past stands in vital relation not only to geology and botany, but to men. Hence it is necessary to consider fully the ruins of the Southwest and the conditions under which the people lived. This is done in Chapters 6 to 10. The ruins and civilization of the Mayas in Yucatan and Guatemala are also important lines of evidence, and in Chapters 15 to 18 the theory is advanced that when the Mayas were in their prime the lowlands of this region were decidedly drier than now.

Petrol Substitutes. B. REDWOOD and V. B. LEWES. (Times Eng. Suppl., July 23, 1913.)—Increased supplies of petrol are now obtained by compressing natural gas so as to condense pentane and hexane, a very light spirit being produced which is suitable for mixing with a heavier spirit to render the latter sufficiently volatile for use in carburettors. Oils of specific gravity 0.8, or a mixture of such oil with 40 to 60 per cent. of petrol, can now be used in special carburettors fitted with a supplementary feed tank containing petrol for starting. The heavier fractions of crude petroleum are converted into motor spirit by "cracking" in contact with iron, and an increase of 30 per cent. in the yield is obtained. The quantity of benzene available for motor spirit from gas works tar in England is only 50,000 gallons per annum, and it is doubtful whether motor spirit can be obtained profitably by distilling coal at low temperatures and "cracking" the naphtha distillates obtained from the tar. The maximum yield obtained at present is 3 gallons of motor spirit per ton of coal carbonized in coke ovens. The only motor spirit obtainable in unlimited quantities is alcohol, which could be made for the purpose and sold at 1 shilling (25 cents) per gallon.

The Heating Value of Gas. (Times Eng., July 19, 1912.)—The committee of the House of Commons on unopposed bills has passed the bill authorizing the South Suburban Gas Company to acquire the undertakings of the Bromley and Crays and the West Kent Gas Companies. The most interesting feature of the bill is the adoption of a test for the calorific value of the gas supplied within the area of the amalgamated company, in substitution of the present penalty test for illuminating power. Penalties are attached for any deficiency in the prescribed standard of calorific value, but no penalty is incurred unless the gross calorific value falls below 475 B.T.U. per cubic foot. The substitution, which has been agreed to by the company on the suggestion of the London County Council, is due to the almost universal adoption of incandescent mantles and to the largely-increased use of gas for heating and cooking purposes.

Application of Low-Pressure Turbines. F. Hodgkinson. (Elect. Journ., x, p. 317.)—Low-pressure turbines are more simple to design and construct on account of the lower temperatures and pressures involved, but much skill is required in their economical application. The three main problems which arise are: (1) Determination of the steam available; this is best made from the indicator cards. (2) What type of governing is to be used: whether the direct centrifugal or indirect electrical. (3) Is the introduction of a low-pressure turbine economically sound, or should the reciprocating engines be displaced by a complete turbine plant? Low-pressure turbine installations are divided into eight classes, each of which is discussed at considerable length. Each class is illustrated diagrammatically, and various practical considerations are brought into notice. The thermal efficiency of an exhaust steam turbine is only about ten per cent.

Radiation Pressure. G. D. West. (Electr. World, lxii, 5, 247.)—A paper read before the Physical Society. The pressure of the radiation emitted by a carbon-filament lamp at a distance of a few centimetres is sufficient to cause a microscopically measurable deflection of the end of a suspended strip of gold or aluminum foil, and by this means the radiation pressure can be calculated, if the weight of the strip is known. The results agree to within about 10 per cent. with the energy content per cubic centimetre as measured by the initial rate of rise of temperature of a copper plate exposed to the radiation. The best results are obtained by working in an atmosphere of hydrogen of 1 cm. to 2 cm. pressure, but good results are obtained with hydrogen at atmospheric pressure. Air at 1 cm. to 2 cm. pressure also gives good results. The method involves no laborious adjustments, and the apparatus is not seriously affected by vibration.

# THE FRANKLIN INSTITUTE

(Proceedings of the Stated Meeting held Wednesday, Nov. 19, 1913.)

HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, November 19, 1913.

PRESIDENT WALTON CLARK in the Chair.

Additions to membership, 31.

Dr. George A. Hoadley, on behalf of the Committee on Science and the Arts, introduced Mr. Halcolm Ellis, of Newark, N. J., who had been recommended by the Institute to the City of Philadelphia for the award of the John Scott Legacy Medal and Premium for his Adding Typewriter. The Chairman presented the medal to Mr. Ellis.

After the transaction of the above Institute business, a joint meeting was held with the American Society of Mechanical Engineers, President Clark and Chairman Yarnall, of the Philadelphia Section, presiding jointly.

Dr. R. H. Fernald, consulting engineer, U. S. Bureau of Mines, and Whitney Professor of Dynamical Engineering of the University of Pennsylvania, presented the paper of the evening on "Producer Gas from Lowgrade Fuels."

The speaker described the results of investigations made by the U. S. Bureau of Mines on the utilization in gas producers of fuels heretofore not regarded as adapted to the economical production of power. Consideration was also given to important factors developed in these investigations, such as the practical elimination of the smoke nuisance, the centralization of power, development and the distribution of power.

The subject was illustrated by lantern slides and numerous specimens of various low-grade fuels.

In the discussion which followed the paper, Messrs. Henderson, Klumpp, Stratton, and others participated.

After a vote of thanks to the speaker the meeting adjourned.

R. B. OWENS,
Secretary.

### COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, November 5, 1913.)

HALL OF THE FRANKLIN INSTITUTE, PHILADELPHIA, November 5, 1913.

Mr. J. A. P. Crisfield in the Chair.

The following reports were presented for final action:
No. 2527.—Norton "Alundum." Edward Longstreth Medal of
Merit. Adopted.

No. 2535.—Tirrill Voltage Regulator. John Scott Award recommended. Adopted.

No. 2543.—Kinkead Shaft Leveling Device. Edward Longstreth Medal of Merit. Adopted.

The following reports were presented for first reading:

No. 2536.—Coolidge's Malleable Tungsten. Investigation deferred.

No. 2537.—Cooper-Hewitt Mercury Rectifier.

No. 2538.—Pohle Air Lift. Advisory. Adopted.

The following applications were accepted for examination:

No. 2587.—Spielman's Cloth Cutting Machine.

No. 2588.—Rice's Gasoline Rock Drills.

The following subjects were recommended for examination:

No. 2589.—The Nitrogen-Filled Tungsten Lamp.

No. 2590.—Butterfield's Automatic Astronomical Calculator.

No. 2591.—Emmett's Electrical Propulsion of Ships.

R. B. OWENS,
Secretary.

## SECTIONS.

Electrical Section.—A joint meeting of the Section and of the Philadelphia Section of the American Institute of Electrical Engineers was held in the Hall of The Franklin Institute on Thursday evening, October 23, 1913, at 8 o'clock.

Mr. H. A. Hornor and Mr. A. R. Cheyney presided jointly.

The minutes of the previous meeting were approved.

Mr. F. W. Peek, Jr., Consulting Engineer, General Electric Company, presented a paper entitled "High-Voltage Engineering," in which he considered some of the problems relating to the insulating of high-tension lines.

The subject was illustrated by lantern slides.

After some discussion, the thanks of the meeting were extended the speaker.

Adjourned.

WILLIAM E. BULLOCK,

Acting Secretary.

Mining and Metallurgical Section.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, October 30, 1913, at 8 o'clock.

Professor A. E. Outerbridge, Jr., occupied the chair.

The minutes of the previous meeting were approved.

Professor Bradley Stoughton, Consulting Metallurgical Engineer, New York City, presented a paper entitled "The Making of Sound Steel Ingots."

Professor Stoughton described the more important processes now employed for eliminating blowholes and impurities in casting ingots, thereby producing high quality material for structural and other purposes.

His paper was illustrated by lantern slides.

After some discussion, the thanks of the meeting were extended the speaker.

Adjourned.

WILLIAM E. BULLOCK,

Acting Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on the evening of November 6, 1913, at 8 o'clock, with Dr. Harry F. Keller in the chair.

The Chairman introduced Dr. Harry C. Jones, Professor of Physical Chemistry in the Johns Hopkins University, who delivered a lecture on "The Present State of Our Knowledge of Solution," in which he discussed the formation of hydrates and other solvates by dissolved electrolytes, as shown by the abnormal depression of the freezing-point, and by optical phenomena, such as absorption spectra and changes in the transparency of solutions. The lecture was illustrated by means of lantern slides.

The paper was discussed at great length; a vote of thanks was extended to Dr. Jones, and the meeting adjourned.

Joseph S. Hepburn, Secretary.

## MEMBERSHIP NOTES.

# Elections to Membership.

(Stated Meeting of the Board of Managers, November 12, 1913.)

#### RESIDENT.

- Mr. W. Asef, 135-B South Forty-ninth Street, Philadelphia, Pa.
- MR. FREDERICK WM. BARKER, JR., Benzol Products Company, Frankford, Philadelphia, Pa.
- MR. EDMOND W. BUREAU, Southeast corner Twenty-third and Westmoreland Streets, Philadelphia, Pa.
- Mr. W. E. Firth, 400 West Chelten Avenue, Germantown, Philadelphia, Pa.
- MR. CHARLES E. MACHOLD, 17 West Phil-Ellena Street, Germantown, Philadelphia, Pa.
- MR. HAROLD MAITLAND, Sun Company, Marcus Hook, Pa.
- Dr. Francis D. Patterson, Harrison Brothers and Company, Inc., 3500 Gray's Ferry Road, Philadelphia, Pa.
- MR. THOMAS C. PINKERTON, The Chemical Laboratories, Inc., Northwest corner Thirteenth and Sansom Streets, Philadelphia, Pa.
- MR. GEORGE RUECK, 37 North Sixty-third Street, Philadelphia, Pa.
- MR. WM. STROBRIDGE, U. S. Cast Iron Pipe and Foundry Company, Burlington, N. J.
- MR. WM. J. THORN, 1439 North Sixty-second Street, Philadelphia, Pa.

#### NON-RESIDENT.

- Mr. J. C. Bannister, National Tube Company, Kewanee, Ill.
- MR. W. N. BEST, II Broadway, New York, N. Y.
- MR. ABRAHAM G. BLAKELEY, P. & R. Coal and Iron Company, Pottsville, Pa.
- Mr. Sterling H. Bunnell, The Griscom-Russell Company, 90 West Street, New York, N. Y.

Mr. A. Christianson, 198 West Pearl Street, Butler, Pa.

Mr. F. H. CLARK, General Superintendent of Motive Power, B. & O. Railroad Company, Baltimore, Md.

Mr. Albert E. Cluett, P. O. Box 666, Troy, N. Y.

Mr. F. J. Cole, 3 Avon Road, Schenectady, N. Y.

PROF. W. L. DUDLEY, Vanderbilt University, Nashville, Tenn.

MR. COLEMAN DU PONT, 27 Pine Street, New York, N. Y.

Mr. A. H. EMERY, Glenbrook, Conn.

Mr. C. N. Forrest, New York Testing Laboratory, Maurer, N. J.

Mr. E. S. Fretz, The Light Manufacturing and Foundry Company, Pottstown, Pa.

Mr. Edwin M. Herr, 140 Hutchinson Avenue, Swissvale, Pa.

Mr. Julius A. Koch, Pittsburgh College of Pharmacy, University of Pittsburgh, Pittsburgh, Pa.

Mr. R. C. McKinney, Niles-Bement-Pond Company, III Broadway, New York, N. Y.

MR. FRANK M. MASTERS, Modjeski & Angier, 101 Park Avenue, New York, N. Y.

Mr. Charles S. Vadner, 2505 South Ninth East, Salt Lake City, Utah.

Mr. Henry H. Vaughan, 8 Weredale Park, Montreal, Canada.

MR. F. W. WESTON, 50 Church Street, New York, N. Y.

# Changes of Address.

MR. WILLARD S. ATKINSON, Westmont, N. J.

Mr. John A. Capp, 1332 Union Street, Schenectady, N. Y.

Mr. Eckley B. Coxe, Jr., Drifton, Pa.

Mr. J. H. Eastwick, The Montevista, Sixty-third and Oxford Streets, Philadelphia, Pa.

Mr. J. H. Granbery, 148 West Eleventh Street, New York, N. Y.

DR. HAROLD HIBBERT, P. O. Box 391, Wilmington, Del.

MR. B. B. MILNER, c/o Mr. H. L. Ingersoll, Assistant to Senior Vice-President New York Central Lines, Grand Central Terminal, New York, N. Y.

Mr. Walter Palmer, West Twenty-fourth Street, Chester, Pa.

MR. PERCIVAL ROBERTS, JR., 717 Commercial Trust Building, Philadelphia, Pa.

# NECROLOGY.

Henry Pemberton, Jr., was born in Philadelphia, September 13, 1855. He was educated at the Western University of Pennsylvania, Pittsburgh, and entered the University of Pennsylvania, Philadelphia, as a special sudent in 1873, receiving a certificate of proficiency in June, 1875. He was chemist for the U. S. Chemical Company, Philadelphia, 1877 to 1883; manager of the Kalion Chemical Company, Philadelphia, 1883 to 1887, and of the Laramie (Wyo.) Chemical Works, 1888. He served as special agent of the eleventh census for the collection of statistics of the chemical industry. He was a member of the American Chemical Society and the Society of Chemical

Industry, and contributed numerous articles on technical subjects to the scientific journals. Mr. Pemberton became a member of the Institute on October 6, 1876, and was made a life member in October, 1890, he served on its Board of Managers from 1891 to 1896, and for many years was a member of the Committee on Library.

Arthur Lincoln Adams, Consulting Hydraulic Engineer, was born at Greensburg, Ind., in 1864, and died at Oakland, Cal., September 17, 1913. He was educated at Hanover, Ind., College, Washburn College, Kansas, and the Kansas State University. He served as engineer of the Burlington and Missouri River Railway, 1886 to 1887; Oregon and Pacific Railroad, 1887 to 1889, and for over ten years practised as a water works expert, having prepared plans for city water works at Dayton, Waitsburg and Colfax, Wash., La Grande and Astoria, Ore. Since 1902 he was in private consulting work. He was a member of the American Water Works Association, the Technical Society of the Pacific Coast, the New England Water Works Association; member and past director of the American Society of Civil Engineers. member and past president of the Pacific Association of Consulting Engineers. He became a non-resident member of the Institute May 11, 1900.

Sir William Henry Preece was born February 15, 1834, near Carnarvon, North Wales, and died in London, November 6, 1913. He was educated at King's College, London, and studied electricity at the Royal Institution under Michael Faraday. During the greater part of his life he was engaged in telegraph work. For many years he was an employee of the Electric Telegraph Company, which ceased its existence in 1870 when the control of the telegraph was taken over by the government. His connection with the Electric Telegraph Company began in 1852, when he entered the office of the late Edwin Clarke, its chief engineer. From 1854 to 1856 he was assistant to Latimer Clarke, and then became superintendent of the southern district. He became superintendent of the electrical system of the London and Southwestern Railroad in 1860, and in 1870 entered the Post Office Service as divisional engineer. He was appointed electrician in 1877, and engineer-inchief and electrician in 1892. He retired from active service in 1899. Sir William visited the United States in 1877 and again in 1884. During the latter visit he was representative of the British Government at the Electrical Conference held under the auspices of The Franklin Institute at Philadelphia. Sir William began experimenting with wireless telegraphy in 1884, and worked out an electro-magnetic system, which was in practical operation between Larvernock, near Cardiff, and Flatholm, an island in the British Channel, a distance of more than three miles. Sir William was past president of the Institution of Electrical Engineers, and for several years president of the Institution of Civil Engineers; was a Fellow of the Royal Society, a member of the Physical Society, the Royal Institution, the Society of Arts, and the British Association for the Advancement of Science. His numerous inventions relate to the telephone. Wheatstone apparatus, the telegraph (duplex, quadruplex, multiplex, and wireless), and safety devices for railways. He was the author of works on telegraphy and telephony, and contributed many papers to scientific publications. He was knighted in 1899. Lt.-Col. George O. Squier, military attaché at the American Embassy, London, expressed to the family of Sir William Preece the sympathy of the members of the Institute and also represented the Institute at the memorial services held at St. Margaret's Church, Westminster, on Tuesday, November 11th.

J. G. Watmough, 2114 Walnut Street, Philadelphia, Pa. Benjamin W. Carskaddon, Lansdowne, Pennsylvania.

#### LIBRARY NOTES.

#### Purchases.

ALEXANDER, WM.—Columns and Struts. 1912.

American Institute of Chemical Engineers.—Transactions, 1912.

Canadian Mining Institute, Journal.—General Index, vol. 1-10. 1913.

Соны, G.—Die Pyrazolfarbstoffe. 1910.

COLVIN, F. H., and F. A. STANLEY.—American Machinist Grinding Book. 1912.

EIFFEL, G.—Resistance of the Air. 1913.

ERMEN, W. F. A.—Materials Used in Sizing. 1912.

FINLAY, G. I.—Introduction to the Study of Igneous Rocks. 1913.

GETMAN, F. H.—Outlines of Theoretical Chemistry. 1913.

GREENE, A. M.—Elements of Heating and Ventilation. 1913.

HELDT, P. M.—The Gasoline Automobile. 2 volumes. 1913.

HOLLEMAN, A. F.—Text-book of Organic Chemistry. Third edition. 1913.

IDDINGS, J. P.-Igneous Rocks. 2 volumes. 1909, 1913.

International Catalogue of Scientific Literature.—C, Physics. 11th annual issue. 1913.

International Geological Congress xii. Canada, 1913.—Coal Resources of the World. 4 volumes. 1913.

Jahrbuch der Chemie.—22ter Jahrgang. 1912.

LORD, N. W., and D. J. DEMOREST.-Metallurgical Analysis. 1913.

MARTIN, G.—Industrial and Manufacturing Chemistry, Organic. 1913.

MARTIN, G.—Triumphs and Wonders of Modern Chemistry. 1913.

Peddie, R. A.—Engineering and Metallurgical Books. 1912.

RYAN, W. T.—Design of Electrical Machinery. 3 volumes. 1912.

Soddy, F.—Interpretation of Radium. 1913.

Sylvester, J. J.—Collected Mathematical Papers. 4 volumes. 1904-1912.

UNWIN, W. C.—Elements of Machine Design. 2 volumes. 1909, 1912.

Webster's New International Dictionary. 1913.

WILSON, H. M., and H. T. CALVERT.—Text-book on Trade Waste Waters.

Zeitschrift für Instrumentenkunde.—General Register 1-30. 1881-1910.

#### Gifts.

- American Iron and Steel Institute, Bureau of Statistics: Statistics of the American and Foreign Iron Trades for 1912. Philadelphia, 1913. (From the Bureau.)
- An Investigation of the Second Law of Thermodynamics, by Jacob T. Wainwright. Chicago, 1913. (From the Author.)
- Atchison, Topeka & Santa Fe Railway Company, 18th Annual Report, 1913. New York, 1913. (From the Company.)
- Australia Bureau of Census and Statistics: Trade and Customs and Excise Revenue for 1912. Melbourne, no date. (From the Bureau.)
- Babcock & Wilcox Company, Steam: Its Generation and Use. 35th edition. New York, 1913. (From the Company.)
- Boston Elevated Railway Company, 16th Annual Report, 1913. Boston, 1913. (From the Company.)
- Chicago, Burlington & Quincy Railroad Company, 59th Annual Report, 1913. Chicago, 1913. (From the Company.)
- Comparative Statistics of Lead, Copper, Spelter, Tin, Aluminium, Nickel, Quicksilver, and Silver. 19th annual issue, 1903–1912. Frankfort-on-Main, 1913. (From American Metal Company.)
- Detroit Twist Drill Company, Catalogue No. 17. Detroit, no date. (From the Company.)
- Electrical and Lighting Engineering, by Henry W. Spang. New York, 1913. (From the Author.)
- Florida East Coast Railway Company, Annual Report 1913. New York, 1913. (From the Company.)
- Great Britain Board of Trade: Report of Strikes and Lock-outs, 1912. Report on Changes in Rates of Wages and Hours of Labour, 1912. London, 1913. (From the Board.)
- Great Northern Railway Company, 24th Annual Report, 1913. No place, 1913. (From the Comptroller.)
- Hannover Technische Hochschule, Programm 1913-1914. Hannover, Germany, 1913. (From the Hochschule.)
- Ingersoll-Rand Company, General Catalogue. New York, 1913. (From the Company.)
- Institution of Civil Engineers of Ireland, Transactions, vol. 39. Dublin, 1913. (From the Institution.)
- Manchester Association of Engineers, Transactions 1912–1913. Manchester, England, 1913. (From the Association.)
- Manchester Statistical Society, The Economic Value of the Ship Canal to Manchester and District, by J. S. McConechy. Manchester, England, 1912. (From the Society.)
- Michigan Department of Labor, 30th Annual Report. Lansing, 1913. (From the Department.)
- National Association of Cotton Manufacturers, Transactions, vols. 93 and 94. Boston, 1913. (From the Association.)
- National Electric Light Association, Proceedings of 36th Convention, 1913. Chicago, 1913. (From the Association.)
  - Vol. CLXXVI, No. 1056—51

- New Zealand Mines Department, Mines Statement, 1912. Wellington, 1913. (From the Department.)
- Northampton Polytechnic Institute, Announcements 1913–1914. London, 1913. (From the Principal.)
- North of England Institute of Mining and Mechanical Engineers, Annual Report 1912-1913. Newcastle-upon-Tyne, 1913. (From the Institute.)
- Oklahoma Geological Survey, Bulletin Nos. 7-11, 15 and 16. Norman, 1911-1912. (From the Survey.)
- Ontario Veterinary College, Report 1912. Toronto, 1913. (From the Ontario Department of Agriculture.)
- Origin of Architectural Design or the Archæology of Astronomy, by Lee H. McCoy. Benton Harbor, Mich., 1912. (From the Author.)
- Pennsylvania Museum and School of Industrial Art, 37th Annual Report, 1913. Philadelphia, 1913. (From the Museum.)
- Smithsonian Institution, Annual Report 1912. Washington, D. C., 1913. (From the Institution.)
- Southern Railway Company, 19th Annual Report, 1913. No place, no date. (From the Company.)
- Spencer Heater Company, Catalogue No. 12. Scranton, no date. (From the Company.)
- Text-book on Highway Engineering, by A. H. Blanchard and H. B. Drowne. New York, 1913. (From Dr. R. B. Owens.)
- Transporter Bridges, by Henry Grettan Tyrrell. Toronto, Can., 1912. (From the Author.)
- United States Coast and Geodetic Survey: Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory near Honolulu, Hawaii, 1911 and 1912. Special Publication No. 16, Triangulation along the West Coast of Florida, by Clarence H. Swick. Washington, D. C., 1913. (From the Department of Commerce.)
- United States National Museum: Bulletin 80, A Descriptive Account of the Building Recently Erected for the Departments of Natural History of the United States National Museum, by Richard Rathbun. Washington, D. C., 1913. (From the Museum.)
- United States Post Office Department: Street Directory of the Principal Cities of the United States. 1908. 5th Edition. Washington, D. C., 1908. (From the Government Printing Office.)
- Wabash Railroad Company, 24th Annual Report, 1913. St. Louis, 1913. (From the Company.)
- Washington University, University Studies, vol. 1, pt. 1, No. 1, July, 1913. St. Louis, 1913. (From the University.)
- Western Australia Geological Survey: Bulletin 44, A Geological Reconnaissance of a Portion of the Southwest Division of Western Australia, by E. C. Saint-Smith. Perth, 1912. (From the Agent General for Western Australia.)

## BOOK NOTICES.

AN INDUCTIVE CHEMISTRY, by Robert H. Bradbury, Ph.D., Head of the Department of Science, Southern High School, Philadelphia. D. Appleton & Co., New York and Chicago.

Among the great number of text-books which are now available for the teaching of chemistry in our secondary schools this is undoubtedly one of the best. While it may be questioned whether certain innovations the author makes in the arrangement and order of the topics, and in the development of the theory, will appeal to every teacher, we know of no other text that so thoroughly covers elementary chemistry, either as an end in itself or as a preparation for colleges and professional schools. Every paragraph gives evidence not only of the author's mastery of the subject, but also of his long teaching experience. Considering the size of the book, it is very remarkable what an amount of accurate and up-to-date information in all branches of chemistry-inorganic, physical, organic, and industrial-may be found between its covers; and all this matter is thoroughly assimilated in the clear and logical exposition. The book is printed in clear type on good paper; the illustrations by the author's wife are clear and very numerous. A series of fine portraits of the great chemists forms an attractive feature of the book.

HARRY F. KELLER.

REGULATION, VALUATION AND DEPRECIATION OF PUBLIC UTILITIES, by Samuel S. Wyer, Mech. and Cons. Engineer. Sears & Simpson Company, Columbus, Ohio, 1913. Thin paper, 314 pp., gilt edged, flexible leather binding. Price, \$5, postpaid.

A compendium of technical, economic, and legal data relating to the regulation of public utilities, including a concise presentation of the principles on which the various regulations are based, and brief discussions of the practical application of these principles. The technical phases of the subject are illustrated by a series of graphical and pictorial representations, the economic data by numerous analytical diagrams, all very carefully prepared and unusually well executed. The legal questions are elucidated by brief citations of authoritative opinion, the various discussions being furthermore clarified by references to a long list of technical publications and citations of judicial opinions by the U. S. Supreme Court, the several U. S. Circuit Courts, the Interstate Commerce Commission, various State courts and public service commissions, and by the British Court of Chancery. A copious index completes the thoroughness of this altogether valuable compilation.

L. E. LEVY.

CHEMICAL GERMAN, by Francis C. Phillips. Easton, Pa., The Chemical Publishing Company, 1913. 241 pages (14 x 22 cm.). Price, \$2.

Most courses in chemistry and chemical engineering require German for admission and include it in their curricula. Nevertheless, graduates of such courses are always unable to read German chemical journals intelligently.

This is merely another instance of the futile character of the instruction usually given in foreign languages. It is likely that hardly one-hundredth of one per cent. of the students who begin French or German ever get far enough to make any actual use of the language. Probably the chief reason for this state of things is that teachers, for some inexplicable reason, invariably lay the accent on learning to speak the language, instead of learning to read it. The ability to speak a foreign language is a mere showy accomplishment of very little practical value. Further, it is an accomplishment which, without residence in the country where the language is spoken, can be acquired only by a miracle. Finally, if the student should, in some extra-natural way, acquire a fluent speaking knowledge, he would begin to lose it at once through lack of practice, and in a few years the loss would be complete.

However that may be, the inability of young chemists to handle German is a serious matter, since the language is about as important to them as English. Professor Phillips thinks that he has discovered a contributing cause of the difficulty in imperfect specialization in the language teaching His book is an attempt to induct the student into the specific vocabulary of chemical science. There are about fifty pages of introductory exercises. The remainder of the book is occupied by selections from the literature of chemistry and by a vocabulary of chemical terms. The material offered is good, in the main, though naturally very unequal in merit. Some selections, like Victor Meyer's account of his discovery of thiophene, are of first-rate historical importance. On the other hand, the sciolistic characterizations of Berthollet and Scheele from Heller's "Geschichte der Physik" are of value only in so far as they show how completely the historian failed to grasp the significance of the work of these great chemists. There are hardly any technological selections.

All in all, the book is a good one. The student who masters it will be able to read the German journals without much difficulty. Without access to the German literature it is impossible for a chemist to inform himself thoroughly upon any topic.

ROBERT H. BRADBURY.

A New Era in Chemistry. Some of the More Important Developments in General Chemistry during the Last Quarter of a Century. By Harry C. Jones, Professor of Physical Chemistry in Johns Hopkins University. New York: D. Van Nostrand Company, 1913. Pp. xii + 326. Price, \$2. In this book the author has traced very briefly the progress of theoretical chemistry during the past twenty-five years, indicating the chief points of difference between the older and the newer chemistry. Professor Jones's personal acquaintance with many of the pioneers of the "New Era" has enabled him to introduce interesting biographical sketches of these scientists and to enliven his book with some entertaining anecdotes.

After an introductory chapter on the condition of chemistry at the dawn of the "New Era" in 1887, the author proceeds to outline the development of the law of mass action, the hypotheses of Van't Hoff, Le Bel and Guye, the phase rule of Gibbs, the views of Van't Hoff and Le Chatelier on

chemical equilibrium, and the modern theory of solution, including the electrolytic dissociation theory of Arrhenius. In another chapter Professor Jones gives a concise summary of the series of investigations conducted in his own laboratory which have established the validity of the solvate theory of solutions.

The recent experimental work of Thomson, Rutherford and Mme. Curie is briefly described, and the bearing of this work upon chemical phenomena is discussed. The chapters devoted to the work of Ostwald and his pupils in the old Leipzig laboratory, in what is known as "Die gute Zeit," are most interesting.

An appendix containing short biographical sketches of Mendeléef, Kekulé, Gibbs, Ramsay, Van't Hoff, Ostwald, and Arrhenius must be ranked as one of the best chapters of the book.

It is to be regretted that the author chose the case of the precipitation of sodium chloride from a saturated solution by dry hydrochloric acid gas as an example of the change in solubility produced by adding to a salt solution an electrolyte with a common ion, since in this particular system complications have been shown to occur. Several typographical errors have been noted, but these are almost inevitable in a first edition and will undoubtedly be corrected in subsequent printings.

As an epitome of recent progress in one branch of chemical science this book should prove of interest to the general reader as well as to the scientific student, especially since it is written in the author's well-known enthusiastic style and escapes the dulness which so often characterizes books of this order.

FREDERICK H. GETMAN.

### PUBLICATIONS RECEIVED.

Mellor, J. W. A Treatise on Quantitative Inorganic Analysis, with Special Reference to the Analysis of Clays, Silicates, and Related Minerals: being vol. i, of a treatise on ceramic industries, by J. W. Mellor, D. Sc. 778 pages, illustrations, plates, 8vo. London, Charles Griffin & Co., Ltd.; Philadelphia, J. B. Lippincott Company, 1913.

Abhandlungen aus dem Gebiete der Technischen Mechanik von Dr.-Ing. Otto Mohr, Geheimer Rat und Professor. Second edition, 567 pages, illustrations, 8vo. Berlin, Wilhelm Ernst and Son, 1914. Price, in paper, 18 marks.

Notions Fondamentales de Chimie Organique par Charles Moureu, membre de l'Institut et de l'Academie de Médicine. Fourth edition, revised, 383 pages, illustrations, 8vo. Paris, Gauthier-Villars, 1913. Price, in paper, 9 francs.

North Carolina Geological and Economic Survey: Economic Paper No. 33, Forest Fires in North Carolina during 1912 and National and Association Coöperative Fire Control, by J. S. Holmes, Forester. 63 pages, 8vo. Raleigh, State Printers, 1013.

Canada, Ministère des Mines, Division des Mines: Bulletin No. 4 (seconde édition), En quête sur les Tourbières et l'industrie de la tourbe a

Canada durant la paison 1909–10 par Aleph Anrep, Jr., expert en Tourbe. 48 pages, illustrations, plates, maps, 8vo. Minéraux industriels et industries minières du Canada par le Personnel de la Division de Mines, Marc Sauvelle, Traducteur. 85 pages, illustrations, plates, maps, 8vo. Rapport sur les dépôts de fer chromé des cantons de l'Est de la province de Quebec par Franz Cirkel, I. M. Traduit de l'Anglais par J. Obalski. 145 pages, illustrations, plates, maps, 8vo. Rapport sur les minerais de Tungstene du Canada par T. L. Walker, M.A., Ph.D. Traduit de l'Anglais par Jobson Paradis. 56 pages, illustrations, plates, 8vo. Ottawa, Imprimerie du Gobernement, 1913.

Konstant auftretende secundäre Maxima und Minima in dem jährlichen Verlauf der meteorologischen Erscheinungen, ix Teil von Dr. E. Van Rijckevorsel. Separatabzug aus Koninklijk Nederlandsch Meteorologisch

Instituut No. 102. 33 pages, tables, 8vo. Utrecht, 1913.

U. S. Bureau of Mines: Miners' Circular 8, First-aid Instructions for Mines, by M. W. Glasgow, W. A. Raudenbush, and C. O. Roberts. 66 pages, illustrations, 8vo. Technical Paper 51, Petroleum Technology 11, Possible Causes of the Decline of Gas Wells and Suggested Methods of Prolonging Yield, by L. G. Huntley. 32 pages, illustrations, 8vo. Washington, Government Printing Office, 1913.

On Some New Multiple Relations of the Atomic Weights of Elementary Substances; and on the Classification and Transformations of Neon and Helium, by Henry Wilde, D.Sc., D.C.L., F.R.S. From volume 57, part iii, of "Memoirs and Proceedings of the Manchester Literary and Philosophical Society, Session 1912–1913," and from the Philosophical Magazine for October, 1913. 2 pamphlets, 8vo.

The Illumination of Street Railway Cars, by L. C. Porter and V. L. Staley. A paper read at a meeting of the Chicago Section of the Illuminating Engineering Society, November 12, 1913. 19 pages, illustrations, 8vo. New

York, Society, 1913.

Temperature of Filaments in Incandescent Lamps. Summer. (Electr. World, 1xii, 5, 245.)—A paper read before the German Illuminating Engineering Society on a new method of determining the true temperature of the filaments in incandescent lamps. If the law for the total radiation is known for a substance, and the radiation constant is also known in absolute units, it is possible to determine from the Joulean heat the true temperature of a filament of given surface, if the total electrical energy supplied to the filament is changed into radiation. For the absolute black body and for bright platinum the radiation laws are exactly known. For other metals the Aschkinass theory must be employed. The authors have experimented with platinum filaments and discuss the various assumptions made in this method.

# CURRENT TOPICS.

Brush-Contact Resistance. Alfred Hay, M. H. Bratt, and J. M. Parish. (Electr. World, Ixii, 5, 245.)—An illustrated account of experiments in brush-contact resistance, the main object of which was to ascertain how far the brush-contact drop is affected by the rotation of the commutator. In the method used care was taken to eliminate the effect of electromotive force in the armature due to imperfect commutation. The conclusion is reached that the brush-contact loss when a machine is running is, for all practical purposes, identical with that which occurs in a stationary armature, so that the loss can be easily determined by measurement with the armature at rest. This result agrees with that of several other experimenters, but differs radically from the results of Gratzmuller.

Application of Oxides Infrequently Used in Glass Manufacture. L. Springer. (Sprechsaal, xlvi, 476, 495, 511, and 525.)— The introduction into glass of the oxides of barium, zinc, magnesium, aluminum, boron, and phosphorus is regarded from the points of view of history, raw material, properties, and application. Barium oxide, first used by Döbereiner at Jena in 1829, is used generally as carbonate, less often as sulphate or nitrate. It increases the specific gravity, refractive index, elasticity, and tenacity of glass, and imparts an attractive surface, but renders it more difficult to work, and also lessens the specific heat. Compared with calcium oxide, it is more expensive and does not impart chemical resistance, in this respect resembling more closely the alkali oxides. Barium glasses fuse more quickly than similar lime glasses. Barium finds its chief application in rolled glass, but is also used in hollow ware, crystal and table glass, and in special glasses, such as the Jena phosphate crown glass, which is essentially a barium metaphosphate containing 28 per cent. BaO and 60 per cent. P<sub>2</sub>O<sub>5</sub>. It can act as a substitute for lead oxide in crystal glasses, a suitable formula being: 4 Na<sub>2</sub>O, 4 BaO, 4 CaO, 36 SiO<sub>2</sub>. In table glass it can replace lime and soda. Zinc oxide, which was used in Belgian factories in the middle of the last century, is introduced as oxide under the names of zinc white. snow white, or crown white; also as zinc blende mixed with Glauber salt, and as calamine. The power of refraction it imparts is less than that produced by lime and much less than by lead and barium. It acts as a basic oxide like magnesia in producing a very low coefficient of expansion, for which reason it is used with boric acid in the manufacture of flashed glass. Zinc glasses have high tensile strength and high resistance, physical and chemical; they tend to crystalliza-

tion and devitrification. They are used chiefly for laboratory and optical purposes. Magnesium oxide is introduced as the carbonate, usually with lime in dolomite, but many feldspars, granites, basalts, etc., contain as much as 10 per cent. MgO. Calcspars, with a magnesia content of 18 per cent., have been used. It has thus found application in glass from the earliest times without contemporary recognition in the literature of the subject. It finds its greatest employment in the French factories. Magnesia increases the fluidity and lowers the viscosity of molten glass and influences fusibility favorably, also the tendency to devitrification and the chemical resistance; the most suitable amount is 2 to 10 per cent. Aluminum oxide renders glass difficultly fusible, but prevents devitrification. It is introduced as clay, bauxite, or feldspar, but the range of raw materials was extended at the end of the last century to include lavas and other similar aluminum silicates. The presence of alumina enables the lime content to be increased without making the glass rough. It makes glass chemically resistant. Alumina is used chiefly in the manufacture of flasks, acid receptacles, etc., the content being 4 to 10 per cent. Boric acid, which is found to be a constituent of old Venetian glass, is introduced as the crystalline hydrate or as borax. It imparts high refractiveness, and in the spectrum reduces the proportion of blue to red, a relation which had previously been exaggerated in flint and crown glass. The coefficient of expansion, the tendency to devitrification, and the melting-point are lowered by high boric acid content. When boric acid is used in conjunction with other acid oxides, the glasses, as for example borosilicate glass, are very resistant to chemical action if the proportion of boric acid be not greater than 10 per cent. Boric acid is employed in crystal and optical glass. Phosphoric acid is introduced as bone ash or other phosphate. It is used for optical purposes, often in conjunction with boric acid. Phosphor-crown glass may contain as much as 70 per cent. P.O.. Arsenic and antimony are used in glass making to assist the progress of chemical reactions and as decolorizers. Jena cylinder glass has a high boric acid content with 4 per cent. Sb.O.

Formation of Hydrochloric Acid in the Distillation of Petroleum. E. Pyhälä. (Petroleum, viii, 1603.)—The corrosion of the iron retorts used in distilling crude petroleum is found to be due to the presence of free hydrochloric acid in the aqueous portion of the distillate. The quantity of the acid was 0.107, 0.043, and 0.026 per cent. in samples of oil containing 29, 12, and 7 per cent. of water respectively. Water, separated from the crude oil and having a specific gravity of 1.1426 at 20° C., yielded 0.33 per cent. of hydrochloric acid when distilled. The acid was not formed until 86 per cent. of the water was distilled over, the temperature then being 125° to 130° C. The acid is probably formed by the decomposition of the chlorides held in solution in the water.

Tantalum as a Cathode Material. G. OESTERHELD. (Z. Elektrochem., xix, 585.)—Tantalum electrodes have a potential difference against sulphuric acid about midway between those of copper and lead. They possess the disadvantage, for many electrolytic purposes, of readily absorbing cathodic hydrogen, which produces a considerable change of structure even when less than 0.1 per cent. is absorbed. The hardness and elasticity of the metal disappear, and it becomes useless as an electrode material. The paper contains measurements relative to the velocity of absorption of hydrogen and to its influence on the overvoltage.

Formation of Methane. L. Vignon. (Comptes Rendus, clvii, 131.)—Methane is formed from water vapor and carbon monoxide when they are heated together to temperatures ranging from 500° C. to 1200° C. in the presence of catalysts—iron, nickel, copper, silica, alumina, magnesia—in greater or less degree, sometimes in considerable quantity. In some cases there is an intermediate formation of carbides, which react with the steam; in others hydrogen is produced, which in presence of the catalyst reacts with the carbon monoxide.

Melting-Points of Refractory Metals. Anon. (Brass World, ix, 10, 349.)—These are recent determinations made by G. K. Burgess and R. G. Waltenberg, and the results are given in the Journal of the Washington Academy of Science. They are:

	C.°	F.°
Titanium	1795	3263
Vanadium	1720	3128
Chromium	1520	2768
Manganese	1260	2300
Iron	1530	2786
Cobalt		2692
Nickel	1452	2545

The determinations were made with a micro-pyrometer, and the metals were melted in hydrogen gas to prevent oxidation. In some cases the metals were melted in an Arsem electric vacuum furnace.

A Refractory Furnace Lining. Anon. (Brass World, ix, 10, 360.)—For certain purposes, a furnace lining of a refractory nature may be made from asbestos and water-glass. It is useful for patching or plugging cracks, as it does not crumble as readily as other similar compositions made from clay. The materials used are:

Fine	asbesto	S													40	pounds
Wate	r-glass				 										бо	pounds

The water-glass is the sodium silicate of commerce, which is soluble in water. The asbestos and water-glass are mixed to a paste with water so that it can be worked. Searchlight. Goerges. (Electr. World, lxii, 5, 245.)—A paper read before the Dresden Electrical Society. It describes tests of a searchlamp with a mirror of 600 mm. diameter and 260 mm. focus, the arc lamp being operated normally at 80 ampères and provided with horizontal carbons. The searchlight was tested in an inside room at 85 volts and 80 ampères, 100 ampères, and 120 ampères, with carbons of different manufacture and of different diameters. With highest concentration of the light the maximum illumination obtained was 850,000 lux. There seems no reason why searchlamps of the largest size cannot be tested in inside rooms of sufficient dimensions. Tests of searchlamps in the free air over long distances will always yield uncertain results, because the transparency of the air varies greatly.

Substitute for Platinum. Anon. (Electr. World, lxii, 5, 217.) —Among the problems encountered by makers of large-size incandescent lamps or rectifying apparatus, not the least important is that of obtaining an air-tight joint between the leading-in wires and the lamp or rectifier bulb. With small units satisfactory results are secured by the use of platinum, of which the coefficient of thermal expansion is the same as that of the glass bulb. In addition to the high cost of platinum, there are several reasons why this method is not equally satisfactory when applied to large units. On page 246 a brief description is given of a recent development in accordance with which tubular leading-in conductors of platinum, copper, or other high-conductivity metal are employed instead of solid wires of platinum. The secret of the process lies in avoiding any appreciable local differences of temperature while making the seal. If the method proves as satisfactory in practice as one is led to believe from the description, it will find wide application in the production of large lamps and rectifiers, with some possibility of causing the substitution of copper for platinum in small incandescent lamps. First the electrical conductor is inserted through an aperture in the glass. glass around the conductor is then strongly heated by means of a blowpipe flame until perfect cohesion has been attained between the glass and the conductor. The seal is now removed from the flame, and when it reaches a dull red heat the leading-in wire and the glass surrounding it are cooled by several immersions in a special bath. The bath may be sperm or other oil, wax or fat, and should be previously warmed slightly. Each immersion should last two or three seconds. The depth of immersion is increased with each successive dip until the seal is completely cooled. If the conductor is required to carry a current of not more than 15 ampères it may be a solid wire, if of more than 15 ampères the conductor should be tubular, filled with an electrical conducting substance. With German and lead glasses, copper, nickel, platinum, etc., may be used, but with Jena glass and fused quartz it is necessary to use platinum.

# INDEX TO VOL. CLXXVI.

Alternating current measurements, the use of the sychronous commutator in (Bedell), 385

Battleship, Electrical equipment of a modern (Hornor), 173

BEDELL, FREDERICK:

The use of the synchronous commutator in alternating current measurements, 385

BERLINER, EMILE:

The development of the talking machine, 189

BOOK NOTICES:

Bradbury, Robert H.: An inductive chemistry, 731

Carnegie Institution of Washington, Publications, 266

Chemical News, General Index, 120 Heald, F. D.: The symptoms of the chestnut tree blight, 462

Jones, Harry C.: A new era in

chemistry, 732 Journal of Agricultural Research,

Molinari, E.: General and industrial chemistry, vol. ii, 460

Pennsylvania Chestnut Tree Blight Commission, Report, 461

Phillips, Francis C.: Chemical German, 731

Thresh, J. C.: The examination of waters and water supplies, 119

U. S. Department of Agriculture, Bureau of Plant Industry, Bul-1etin, 285, 598

Wyer, Samuel S.: Regulation, valuation and depreciation of public utilities, 731
BRADBURY, ROBERT H.: Colloids and

crystals, the two worlds of matter, 319

Bridges, design of large (Modjeski), 239

Bridges, proportioning of long-span truss and catilever (Mayer), 645

CAMERON, FRANK K .: Kelp and other sources of potash, 347

Carnegie Institution of Washington Notes, 715

Chemistry of humus (Jodidi), 565 Cholesterol, Biochemical studies of (Hepburn), 405

COBLENTZ, WM. W.: Further experiments on bismuth thermopiles,

Colloids and crystals (Bradbury), 319

Commutator, synchronous, The use of the, in alternating current measurements (Bedell), 385

Crystals, Colloids and (Bradbury), 319

222, 228, 229, 282, 302, 318, 336, 340, 383, 384, 452, 455, 456, 464, 466, 574, 586, 601, 643, 644, 676, 714, 721, 722, 734, 735

Dielectric properties of non-conductors (Thomas), 283

Electric field distribution (Franklin),

61 Electrical engineering, High-voltage (Peek), 611

Electrical equipment of a modern battleship (Hornor), 173

Electrical propulsion of ships (Em-

met), 43
Electricity, Relation of matter to (Goodspeed), 303
EMMET, W. L. R.: The electrical propulsion of ships, 43

Engineering, High-voltage (Peek),

Engineering, The imaginative faculty in (Randolph), 201

Fire alarm, A new automatic (Fitz-

Gerald), 575 Fitz Gerald, F. A. J.: A new automatic fire alarm, 575
FRANKLIN, W. S.: Notes on electric

field distribution, 61 FRANKLIN INSTITUTE:

Award of the Elliott Cresson Medal to distinguished scientists, 101

Committee on Science and the Arts, Abstract of proceedings at meetings, June 4, 1913, 113: September 3, 1913, 457; October 1, 1913, 503; November 5, 1913, 723

Library notes, 116, 224, 337, 458, 595, 728

Membership notes, 114, 223, 457, 594. 725

Sections, Abstracts of proceedings of meetings, 593, 724

Special meeting, proceedings, Oc-

tober 2, 1913, 591 Stated meetings, proceedings, October 5, 1913, 592; November 19, 1913, 723

Gases, Industrial combustible (Rusby), 1

GOODSPEED, ARTHUR WILLIS: The relation of matter to electricity, 303

Hepburn, Joseph SAMUEL: Biochemical studies of cholesterol,

High-voltage engineering (Peek),

HORNOR, H. A.: The electric equip-

ment of a modern battleship, 173 HUMPHREYS, W. J.: Volcanic dust and other factors in the production of climatic changes, and their possible relation to ice ages, 131.

HUMPHREYS, W. J.: Volcanic dust (correction), 465

Humus, Chemistry of (Jodidi), 565 HYDE, EDWARD P.: The Physical Laboratory of the National Elec-tric Lamp Association, 77

Imaginative faculty in engineering (Randolph), 201

The chemistry of Jodidi, S. L.: humus, with special reference to the relation of humus to the soil and to the plant, 565

Jones, Harry C.: Evidence bearing on the solvate theory of solution, 479, 677

Kelp and other sources of potash (Cameron), 347

Laboratory, Physical, of the National Electric Lamp Association (Hyde), 77

Maintenance-of-way department railroad testing plant (Milner), 207

Matter, Relation of, to electricity

(Goodspeed), 303 MAYER, JOSEPH: Proportioning of long-span truss and cantilever bridges, 645

MILNER, B. B.: A maintenance-ofway department railroad testing plant, 207 ·

Modjeski, Ralph: Design of large bridges with special reference to the Quebec bridge, 239

National Electric Lamp Association, The Physical Laboratory of the (Hyde), 77

Noble, Alfred: The railway tunnels of New York City (correction), 224

Non-conductors, Dielectric properties of (Thomas), 283

PEEK, F. W., JR.: High-voltage engineering, 611

PENROSE, R. A. F., JR.: The Twelfth International Geological Congress, 583 Potash, Kelp and other sources of

(Cameron), 347

Publications received, 121, 227, 339, 462, 599, 733

Quebec bridge (Modjeski), 239

Railroad testing plant, A mainten-

ance-of-way (Milner), 207 Railway tunnels of New York City (correction) (Noble), 224 RANDOLPH, ISHAM: The imaginative

faculty in engineering, 201 Rusby, J. M.: Industrial combustible

gases, I

Ships, Electrical propulsion of (Emmet), 43 Solution, The solvate theory of,

Evidence bearing on (Jones), 479, 677

Solvate theory of solution, Evidence bearing on the (Jones), 479, 677

Talking machine, The development of the (Berliner), 189

Thermopiles, bismuth, Further experiments on (Coblentz), 671

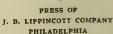
THOMAS, PHILLIPS: The dielectric properties of non-conductors, 283

Twelfth International Geological Congress (Penrose), 583

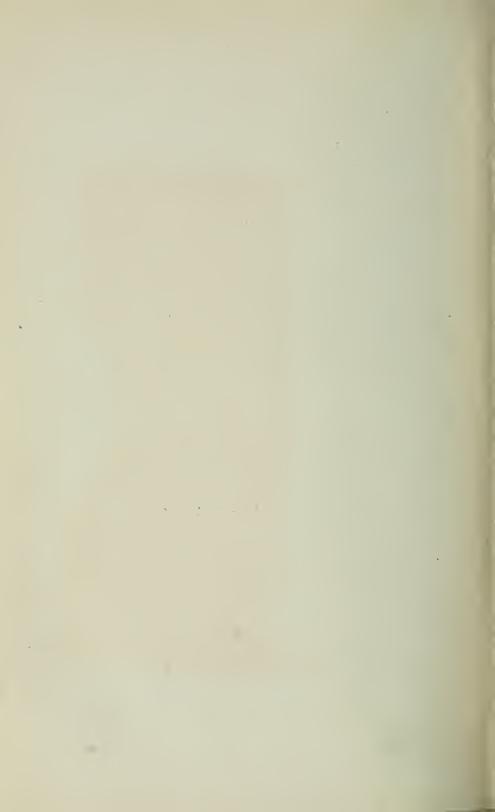
U. S. Bureau of Standards Notes, 95, 219, 329, 453, 587, 711

Volcanic dust and other factors in the production of climatic changes and their possible relation to ice ages (Humphreys),

Volcanic dust (correction) (Humphreys), 465







T 1 F8 v.176

Franklin Institute, Philadelphia Journal



Engineering

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY

ENGIN STORAGE

